

SOUTHERN CALIFORNIA PARTICLE SUPERSITE

Progress Report for Period April 1, 2004 – June 30, 2004

United States Environmental Protection Agency

Principal Investigator: John R. Froines, Ph.D., UCLA School of Public Health

Co-Principal Investigator: Constantinos Sioutas, Sc.D., USC School of Engineering

1. Introduction

The overall objective of the Southern California Particle Supersite is to conduct research and monitoring that contributes to a better understanding of the measurement, sources, size distribution, chemical composition and physical state, spatial and temporal variability, and health effects of suspended particulate matter (PM) in the Los Angeles Basin (LAB). This report addresses the period from April 1, - June 30, 2004. It is divided into 10 sections, each addressing a specific research area. Furthermore, a major portion of the information included in this report has been either submitted or accepted for publication in peer-reviewed journals. Below is a list of manuscripts either submitted or accepted for publication, which was produced through the Southern California Supersite funds and in which the EPA Supersite program has been acknowledged.

2. Publications

The Southern California Particle Supersite has been acknowledged so far in the following publications:

1. Misra, C., Geller, M., Sioutas, C and Solomon P. “Development and evaluation of a continuous coarse particle monitor”. *Journal of Air and Waste Management Association*, 51:1309-1317, 2001
2. Geller, M.D., Kim, S. Misra, C., Sioutas, C., Olson, B.A and Marple, V.A. “Methodology for measuring size-dependent chemical composition of ultrafine particles “ *Aerosol Science and Technology*, 36(6): 748-763, 2002

3. Misra, C., Kim S., Shen S. and Sioutas C. "Design and evaluation of a high-flow rate, very low pressure drop impactor for separation and collection of fine from ultrafine particles". *Journal of Aerosol Science*, 33(5): 735-752, 2002
4. Li, N., Kim, S., Wang, M., Froines, J.R., Sioutas, C. and Nel, A. "Use of a Stratified Oxidative Stress Model to Study the Biological Effects of Ambient Concentrated and Diesel Exhaust Particulate Matter". *Inhalation Toxicology*, 14(5): 459-486, 2002
5. Zhu, Y., Hinds, W.C., Kim, S and Sioutas, C. "Concentration and Size Distribution of Ultrafine Particles near a Major Highway". *Journal of Air and Waste Management Association*, 52:1032-1042, 2002
6. Singh, M., Jaques, P. and Sioutas, C. "Particle-bound metals in source and receptor sites of the Los Angeles Basin". *Atmospheric Environment*, 36(10): 1675-168, 2002
7. Kim, S., Shi, S., Zhu, Y., Hinds, W.C., and Sioutas, C. "Size Distribution, Diurnal and Seasonal Trends of Ultrafine Particles in Source and Receptor Sites of the Los Angeles Basin". *Journal of Air and Waste Management Association*, 52:174-185, 2002
8. Eiguren-Fernandez A., Miguel A.H, Jaques, P. and Sioutas, C. "Evaluation of a Denuder-MOUDI-PUF Sampling System to Determine the Size Distribution of Semivolatile Polycyclic Aromatic Hydrocarbons in the Atmosphere". *Aerosol Science and Technology*, 37: 201-209, 2003
9. Fine, P.M., Hering, S.V., Jaques P.A. and Sioutas, C. "Performance Evaluation and Field Use of a Continuous Monitor for Measuring Size-Segregated PM_{2.5} Particulate Nitrate". *Aerosol Science and Technology*, 37: 342-354, 2003
10. Shen, S., Zhu, Y., Jaques PA and Sioutas C. "Evaluation of the SMPS-APS system as a Continuous Monitor for PM_{2.5} and PM₁₀". *Atmospheric Environment*, 36, 3939-3950, 2002
11. Zhu, Y., Hinds, W.C., Kim, S., Shen, S. and Sioutas, C. "Study on Ultrafine Particles and other Vehicular Pollutants near a Busy Highway". *Atmospheric Environment*, 36, 4375-4383, 2002.
12. Misra, C., Geller, M.D., Solomon, P.A. and Sioutas, C. "Development of a PM₁₀ Inertial Impactor for Coarse Particle Measurement and Speciation." *Aerosol Science and Technology*, 37:271-282, 2003
13. Zhu, Y., Hinds, W.C., Kim, S., Shen, S. and Sioutas, C. "Seasonal Trends of Concentration and Size Distributions of Ultrafine Particles Near Major Freeways in Los Angeles". *Aerosol Science and Technology*, 38, 5-13, 2004.

14. Lippmann, M., Frampton, M., Schwartz, J., Dockery, D., Schlesinger, R.B., Koutrakis, P., Froines, J.R., Jack Finkelstein, J., Godleski, J.J., Koenig, J., Larson T., D., Liu, S.D., Oberdörster, D., Peters, A., Sarnat, J., Sioutas, C., Utell M. "The EPA'S PARTICULATE MATTER (PM) Health Effects Research Centers Program : A Mid-Course (2 1/2 year) Report of Status, Progress, and Plans" Environmental Health Perspectives, 111 (8): 1074-1092, 2003.
15. Gong, H.Jr, Linn, W.S., Sioutas, C., Terrell S.L., Clark, K.W., Anderson K.R and Terrell, L. "Controlled Exposures of Healthy and Asthmatic Volunteers to Concentrated Ambient Fine Particles in Los Angeles". Inhalation Toxicology, 15(4), 305-325, 2003
16. Li, N., Sioutas, C., Froines, J.R., Cho, A., Misra, C and Nel, A., "Ultrafine Particulate Pollutants Induce Oxidative Stress and Mitochondrial Damage" Environmental Health Perspectives, 111 (4), 455-460, 2003
17. Chakrabarti, B., Singh, M and Sioutas C. "Development of a Continuous Monitor For Measuring the Mass Concentration of Ultrafine PM." Aerosol Science and Technology, 38, 239-252, 2004.
18. Jaques, P.A., Ambs, J.L. and Sioutas, C. "Field Evaluation Of The Differential TEOM® Monitor For Continuous PM_{2.5} Mass Concentrations ". Aerosol Science and Technology, 38, 49-59, 2004.
19. Singh, M., Misra, C., and Sioutas, C. "Field Evaluation of a Particle Monitor for Size-Dependent Measurement of Mass and Chemical Composition of Individual Exposures to PM". Atmospheric Environment, [37\(34\)](#), 4781-4793, 2003.
20. Misra, C., Fine, P.M., Singh, M. and Sioutas, C. "Development and Evaluation of an Ultrafine Particle Concentrator Facility for Human Exposures". Aerosol Science and Technology, 38, 27-35, 2004.
21. Fine, P.M., Si, S., Geller, M.G., and Sioutas, C. "Inferring the Sources of Fine and Ultrafine PM at Downwind Receptor Areas in the Los Angeles Basin Using Multiple Continuous Monitors". Aerosol Science and Technology, 38, 182-195, 2004.
22. Chakrabarti, B., Fine, P.M., Delfino R.J. and Sioutas C. "Performance Evaluation of an active personal DataRAM PM_{2.5} mass monitor (Thermo Anderson pDR-1200) designed for continuous personal exposure measurements" Atmospheric Environment, 38(20), 3329-3340, 2004.
23. Yu, R.C., Teh, H.W., Sioutas, C. and Froines, J.R. "Quality Control of Semi-Continuous Mobility Size-Fractionated Particle Number Concentration Data". Atmospheric Environment, 38(20), 3341-3348, 2004.

24. Miguel, A.H., Eiguren-Fernandez, A., Jaques, P.A., Mayo, P.R. and Sioutas, C. "Seasonal variation of the particle size distribution of polycyclic aromatic hydrocarbons and of major aerosol species in Claremont, California" *Atmospheric Environment*, 38(20), 3241-3251, 2004.
25. Geller, M.D., Fine, P.M. and Sioutas C. "The Relationship Between Real-Time and Time-Integrated Fine and Coarse Particle Concentrations at an Urban Site in Los Angeles, CA". *Journal of Air and Waste Management Association*, in press, November 2003
26. Sardar, S.B., Fine P.M., Jaques, P.A and Sioutas. C. "Seasonal and Spatial Variability of the Size-Resolved Chemical Composition of PM₁₀ in the Los Angeles Basin" Submitted to *Journal of Geophysical Research*, May 2004
27. Gong, H., Jr., Linn, W.S., Terrell, S.L., Clark, K.W., Geller, M.D and Sioutas, C. "Altered Heart Rate Variability In Asthmatic and Healthy Volunteers Exposed to Concentrated Ambient Coarse Particles". *Inhalation Toxicology*, 16(6), 335-343, 2004.
28. Jaques, P.A., Ambs, J.L., Hering, S.V., Fine, P.M. and Sioutas, C. "Field Assessment of the Dynamics of Particulate Nitrate Vaporization Using Differential TEOM[®] and Automated Nitrate Monitors ". *Atmospheric Environment*, in press, October 2003
29. Fine, P.M., Chakrabarti, B, Krudysz M., Schauer J.J. and Sioutas, C. "Seasonal, Spatial, and Diurnal Variations of Individual Organic Compound Constituents of Ultrafine and Accumulation Mode PM in the Los Angeles Basin". *Environmental Science and Technology*, 1296 – 1304, April 2004.
30. Sioutas, C., Pandis, S., Allen, D.T. and Solomon, P.A. "Special issue of *Atmospheric Environment* on findings from EPA's particulate matter Supersites program". *Atmospheric Environment* 38(20), 3101-3106, 2004.
31. Sardar, S.B., Fine P.M., and Sioutas. C. "The Relationship Between Particle Number and Co-pollutant Concentrations in the Los Angeles Basin" *Journal of Air and Waste Management Association*, accepted for publication, January 2004
32. Zhang, K.M., Wexler, A.S., Zhu, Y., Hinds, W.C. and Sioutas, C. "Evolution of Particle Number Distributions Near Roadways. Part II: The "Road-to-Ambient Process". *Atmospheric Environment*, in press, July 2004.
33. Miguel, A.H., Cho A.K., Sioutas C., Schmitz, D.A., Kumagai Y., Misra C., Singh M., and Froines, J.R. "DTT Activity Assay for Measurement of the Oxidative Stress Inducing Capacity of Polycyclic Aromatic Compounds in the Atmosphere". Submitted to *Polycyclic Aromatic Compounds*, November 2003.

34. Zhao, Y., Bein, K.J., Wexler, A.S., Misra, C., Fine, P.M. and C. Sioutas, C. "Using a Particle Concentrator to Increase the Hit Rates of Single Particle Mass Spectrometers". Submitted to Journal of Geophysical Research, January 2004
35. Sardar, S., Fine, M., Mayo, P.R. and Sioutas, C. "Size Fractionated Chemical Speciation Measurements of Ultrafine Particles in Los Angeles Using the NanoMOUDI". Submitted to Environmental Science and Technology, April 2004
36. Phuleria, H., Fine, P.M., Zhu, Y. and Sioutas, C. "Characterization of Particulate Matter and co-Pollutants During the Fall 2003 Southern California Fires". Journal of Geophysical Research, in press, May 2004
37. Cho A.K., Sioutas C., Schmitz, D.A., Kumagai Y., Singh M., Miguel A.H and Froines, J.R. "Redox activity of airborne particulate matter (PM) at different sites in the Los Angeles Basin" Submitted to Environmental Research, May 2004
38. Lee, J.H., Hopke, P.K., Holsen, T.M., Wilson, W.E., Sioutas, C. and Ambs, J.L. "Performance Evaluation of Continuous PM_{2.5} Mass Concentration Monitors". Submitted to Journal of Aerosol Science, February 2004.
39. Khlystov, A., Zhang, Q., Jimenez, J.L., Stanier, C.O., Pandis, S., Wornop, D.R., Misra, C., Fine, P.M. and Sioutas, C. "On Concentrating Semi-volatile Aerosols Using Water-Based Condensation Technology" Submitted to Journal of Geophysical Research, February, 2004.
40. Zhu, Y., Hinds, W., Krudysz M., Kuhn, T., Froines, J.R., and Sioutas, C." Penetration of freeway ultrafine particles into indoor environments; I. Ultrafine particles and co-pollutants". Submitted for publication to Journal of Aerosol Science, June 2004.
41. Kuhn, T., Zhu, Y., Hinds, W., Krudysz M., Fine, P.M., Froines, J.R., and Sioutas, C." Penetration of freeway ultrafine particles into indoor environments; II. Volatility properties." Submitted for publication to Journal of Aerosol Science, June 2004.

3. PIU Sampling Location and Status

A key feature of our Supersite activities has been in the ability to conduct state-of-the-art measurements of the physiochemical characteristics of PM in different locations of the Los Angeles basin (LAB). We originally proposed a 2.5-year repeating cycle of measurements at five locations. Each location has been scheduled to sample during a period of intense photochemistry (defined approximately as May–October) and low photochemical activity (defined as the period between November–April). During the period of this progress report, we've continued PM sampling with the Particle Instrumentation Unit (PIU) at the University of Southern California (USC), the fifth Southern California Supersite location, beginning September 2002. The site is located about one mile directly south of downtown Los Angeles and the 10 Freeway, which runs east to west, and is about 100 meters directly east of the 110 Freeway. The site is embellished with typical urban sources: centralized within a major congested urban center; adjacent to several 2–7 story buildings; adjacent to pedestrian and local traffic as well as central arteries; and near building and road construction projects. Since the site is about 15 miles directly east north east of the ocean, prevailing winds are primarily from the west and southwest during most of the daytime when mobile and stationary emission sources may be expected to predominate. However, the nearby relatively large buildings can also disturb the winds, affecting urban canyon and wake properties. These factors consist of turbulent winds and updrafts that may confound local measurements of regional wind trajectories, and increase the delivery of local sources (e.g., construction debris, and larger settled particles from road related vehicle wear-and-tear) in addition to the close-by 110 Freeway. Several studies are being conducted as we enter the third quarter at the USC site to investigate local source contributions in addition to the regional transported emissions that may generally come from the west freeways.

We have completed all Metal/Element speciation, Ion, and EC/OC analysis for integrated samples, through to the end of May. In early June 2003, we finalized size integrated on-line measurements of particulate nitrate and carbon using the Integrated Collection and Vaporization System (ICVS) developed by Aerosol Dynamics Inc. Additionally, paired semi-continuous PM_{2.5} measurements using a prototype Differential TEOM, designed to measure “non-artifact” laden mass, has been completed. Two continuous BAM monitors continue to operate: one, with the standard PM_{2.5} inlet, the second with an ultrafine inlet (designed at the USC lab). Coupled with our USC-TEOM coarse monitor, time-integrated mass measurements are being compared to those by our SMPS-APS, MOUDI, Partisol, and other filter mass samplers for longer sample integrals, overall, resulting in paired integrated semi-continuous, diurnal, and 24-hour mass measurements of coarse, fine, and ultrafine PM.

We have continued to make our mobile particle trailer available for co-located exposure studies. The following health studies have been supported by the Supersite measurements: In vitro studies undertaken by Drs. Andre Nel and Arthur Cho (UCLA) investigating the hypotheses that organic constituents associated with PM, including quinines, other organic compounds (PAHs, nitro-PAHs, and aldehydes/ketones) and metals are capable of generating reactive oxygen species (ROS) and acting as electrophilic agents. These are ongoing studies. Animal inhalation toxicology studies using Concentrated Ambient Particulates (CAP) investigating the

hypotheses that atmospheric chemistry is important in the toxicity of PM and co-pollutants, airway injury and cardiovascular effects will be greater at receptor sites downwind of source sites along the mobile source trajectory in the Los Angeles basin. Led by Drs. Harkema (University of Michigan), Kleinman (UC Irvine), Froines, and Nel (UCLA), these co-located studies have commenced during our first month at the USC site and have continued periodically to the present. A demonstrative-level cooperative project of the California Air Resources Board and the Supersite was initiated during the winter of 2003 to evaluate the nature of PM and gaseous pollutants in various microenvironments of Southern California, especially those impacted by vehicular traffic. Gaseous pollutants evaluated included carbon monoxide, carbon dioxide, and oxides of nitrogen using advanced monitoring equipment including ultrafine PM counters and sizers as well as carbon, PM 2.5, and PAH monitors placed in an electrically powered Toyota RAV4. Data reporting resolution was one minute or less with operations of the study closely linked to the Supersite, its instrumentation and staff. In conjunction with this study, the South Coast Air Quality Management District (SCAQMD) has provided instruments to monitor oxides of nitrogen, ozone and carbon monoxide. These instruments were removed from the site in May 2004.

4. Characterization of PAH and PAH-Derivatives

Janet Arey, Fabienne Reisen, and William P. Harger
Air Pollution Research Center
University of California, Riverside

Work Conducted in the Last Quarter

In August, 2002 and January, 2003 joint field sampling was conducted by researchers from UCR (Reisen and Arey, 2004, submitted for publication) and USC (Fine et al., Environ. Sci. Technol., Vol. 38, pp. 1296-1304, 2004) with samples collected at two sites (USC and UCR) and during two seasons. We have received from Drs. Fine and Sioutas the extracted, size-fractionated samples collected at USC and UCR in August, 2002 and January, 2003. We have received approximately 50% of each accumulation (0.18 – 2.5 μm) mode and ultrafine (diameters <0.18 μm) mode particle sample. We spiked the samples with deuterated 1-nitropyrene and benzo[b]fluoranthene and have now completed fractionation of the samples by HPLC in preparation for GC/MS analysis by negative ion methane chemical ionization for the nitro-PAHs and positive ion methane chemical ionization (and/or electron impact ionization) for the PAHs. It will be interesting to determine if the distribution of 2-nitrofluoranthene, an atmospheric reaction product of radical-initiated atmospheric reactions of fluoranthene, between the accumulation mode and ultrafine particles is similar to the reported distribution (Fine et al., Environ. Sci. Technol., Vol. 38, pp. 1296-1304, 2004) of phthalic acid.

Future Work

The 32 samples from USC and UCR will be analyzed by GC/MS for 2-nitrofluoranthene, 1-nitropyrene and 2-nitropyrene. PAH analyses will also be conducted on each sample to allow quantification of the fraction of the sample extracts delivered to UCR.

5. Coupling a particle concentrator with a single particle mass spectrometer to increase particle hit-rates

Y. Zhao, K. J. Bein, A.S. Wexler, C. Misra, P.M. Fine, and C. Sioutas

This project has been submitted to the JGR-Atmospheres Supersites special issue as:

FIELD EVALUATION OF THE VACES PARTICLE CONCENTRATOR COUPLED TO THE RSMS-3 SINGLE PARTICLE MASS SPECTROMETER

Summary

A field evaluation of the Versatile Aerosol Concentration Enrichment System (VACES) coupled to a Rapid Single-particle Mass Spectrometer (RSMS-3) was conducted as part of the U.S. Environmental Protection Agency (EPA) Supersite program in Pittsburgh during March of 2002. The primary goal was to increase the particle hit-rate of the RSMS-3 by increasing the particle concentration in the air it is sampling. This will allow more rapid collection of data and thus, shorter sampling time periods. Hit rate increases were measured and any potential particle composition changes introduced by the VACES were examined in the single particle mass spectra.

Introduction

A rapid single particle mass spectrometer (RSMS) was developed at the University of California, Davis and the University of Delaware [Phares et al., 2002] for measuring the size and chemical composition of individual atmospheric fine and ultrafine single particles. The second generation of the single particle mass spectrometer, RSMS-2, was deployed at the U.S. Environmental Protection Agency (EPA) Supersite in Atlanta in August 1999 [Rhoads et al., 2003] and in Houston from August 23 to September 18, 2000 [Phares et al., 2003]. In Houston, transient plumes of ultrafine particles that were present at the site for short duration were detected because of the instrument's fine temporal resolution and its ability to run continuously for a period of time. The RSMS-2 was modified to its third generation, RSMS-3, in 2001. In comparison with RSMS-2, there are two major improvements in RSMS-3: (1) both positive and negative ions can be detected and (2) two digitizer channels are combined to record each ion polarity signal to increase the spectral dynamic range. The RSMS-3 was installed at the U.S. EPA Supersite in Pittsburgh. A quarter of million single particle mass spectra were analyzed over a one-year period from September 2001 to October 2002. Results indicate that a rich array of multi-component ultrafine particles were present [Bein et al., 2004].

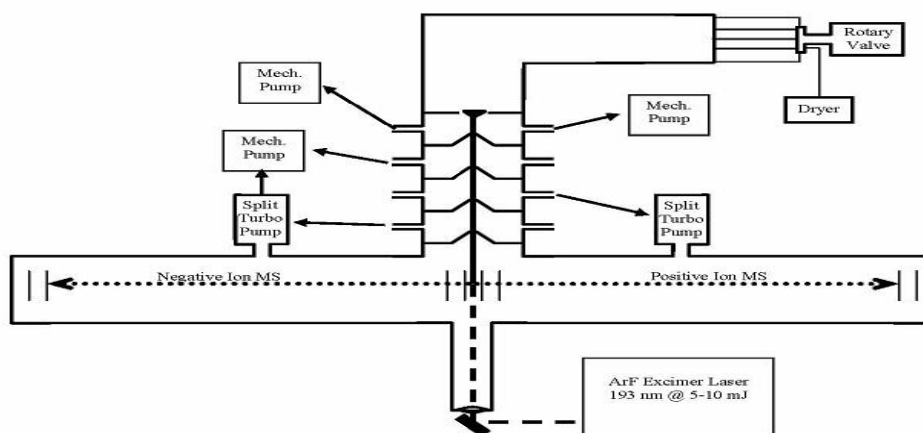
A disadvantage of the RSMS-3 single particle instrument is its insufficient hit rate for all but polluted urban conditions. Laboratory tests showed that the detection efficiency of RSMS was about one in a million and varied with particle size, shape, and composition [Kane and Johnston, 2000, Phares et al., 2002]. In order to increase the RSMS hit rate for cleaner conditions and therefore to broaden its applicability, several methods are under consideration. The goal is to either increase the sampling efficiency without changing its sizing ability or concentrate particles before they enter the instrument. Theoretical work shows that the hit rate may be increased by more than 10 times using a new inlet system with capped cone structure [Middha and Wexler, 2003]. Another way to increase the hit rate is to introduce a particle concentrator to the sampling inlet of the RSMS-3 mass spectrometer.

A particle concentrator (Versatile Aerosol Concentration Enrichment System, VACES) has been developed at the University of Southern California and deployed in many field experiments [Sioutas et al., 1999; Kim et al, 2001a and 2001b]. In its optimum configuration, VACES concentrates fine particles, including the ultrafine mode, by a factor up to 30, depending on the ratio of total-to-minor flow rates of the virtual impactor [Sioutas et al., 1999, Kim et al, 2001a and 2001b]. Evaluation of the VACES was previously performed in both laboratory and field and the results are described in a great detail by Kim et al [2001a and 2001b]. The ability of the VACES to concentrate particles has been laboratory tested using different type of particles, including polystyrene latex (PSL), silica beads, ammonia sulfate, and ammonia nitrate, in the size range from 50 to 1900 nm and at three minor flow rates of 7, 10, and 20 lpm with the major intake flow rate of 220 lpm. TSI Condensation Particle Counter (CPC) was used to measure the number concentration of the original aerosols at upstream and concentrated aerosols at the downstream of the VACES. TSI Scanning Mobil Particle Sizer (SMPS) was used to measure the size distribution of those aerosols. The resulting enrichment factors (ratio of downstream aerosol number concentration to upstream) were very close to the ideal values (ratio of total-to-minor flow rate) and the aerosol size distribution was fairly well preserved during the concentration enrichment process. Hygroscopic aerosols, such as ammonium sulfate and ammonia nitrate were concentrated as efficiently as hydrophobic PSL particles [Kim et al, 2001a]. Field evaluations of the VACES were conducted outdoors in Southern California [Kim et al., 2001b], where measurements of concentration-enriched aerosols were compared to direct ambient measurements made with Micro-orifice Uniform Deposit Impactor (MOUDI). Downstream and upstream measurements showed very good agreement (correlation coefficient $r^2=0.80$ for coarse particles, 0.66 for PM_{2.5} nitrate, 0.84 for PM 2.5 sulfate, and 0.94 for ultrafine elemental carbon). Averaged concentration enrichment of those aerosols was very close to the ideal values. These experimental results indicated that the concentrator does not distort the size distribution of the original ultrafine aerosols based on bulk measurements of particle chemical composition.

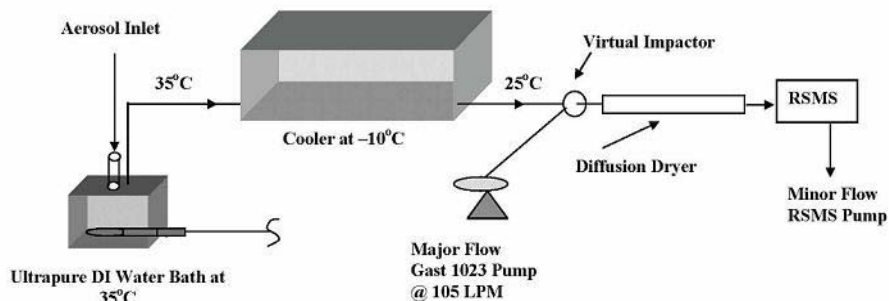
Methods

Below is a schematic of the RSMS-3 instrument. The RSMS-3 consists of a Nafion dryer, a rotary valve orifice bank, an inlet system, two liners jointed with a source region, two Microchannel Plate (MCP) detectors, and an UV ArF Excimer laser. Sample air with particles passes through a dryer and a rotary valve orifice bank and then arrives at the inlet system composed of an aerodynamic lens with four vacuum stages. A 3 lpm carrying dry air passes through the dryer and removes primarily water vapor from the sample. The orifice bank controls inlet pressure. The inlet system creates a particle beam with a narrow particle size range and

skims off most of the gas. The optimum particle size that is focused depends on the upstream pressure, which is controlled by the rotary valve orifice bank. A 193 nm pulsed UV laser beam from an ArF Excimer laser is aligned coaxially with the particle beam by a 45° folding-aligning mirror and focused at the source region by a lens. When the laser beam hits a particle in the source region, the particle is ablated and ionized. Positive ions are accelerated by an electric field and fly inside the liner to the MCP detector on the positive side of the instrument. Negative ions fly in the opposite direction and are detected by another MCP on the negative side. There are nine orifices in the orifice bank, so RSMS-3 can measure nine particle sizes (from 18 nm to 1.1 μm).



The next figure below shows a schematic of the VACES fine plus ultrafine particle concentrator. The VACES consists of a sample line, a saturation-condensation system, a virtual impactor, and a diffusion dryer. Sample air is drawn through the sample line into a 35°C saturation chamber above a warm DI water bath where particles and air are humidified. This warm saturated aerosol is then introduced into a section cooled by 10°C, thereby supersaturating the air and causing rapid condensation and particle growth. A virtual impactor concentrates the particles in its minor flow, which is then dehydrated so the particles return to their original sizes by means of a series of diffusion dryers. Particle enrichment by the VACES concentrator depends on the ratio of the virtual impactor's total-to-minor flow rates [Sioutas et al., 1999, Kim et al., 2001a]. The principle of a virtual impactor is similar to that of an inertial impactor; both methods use particulate inertia to separate particles from gases, but in a virtual impactor, particles are injected into an open collection probe rather than onto a collection medium. A fraction of the total flow, referred to as the minor flow (typically 10%-20% of the total flow), is allowed to pass through the probe, leaving particles larger than the cut-point contained in a small fraction of the initial gases. The cut-point of the virtual impactor used in VACES was 2.5 μm . In this experiment, the minor flow of the concentrator was directly connected to the sample port of the RSMS-3 mass spectrometer. The two instruments were operated at their original configurations, as described in the previous paragraphs in this section, without any modifications.

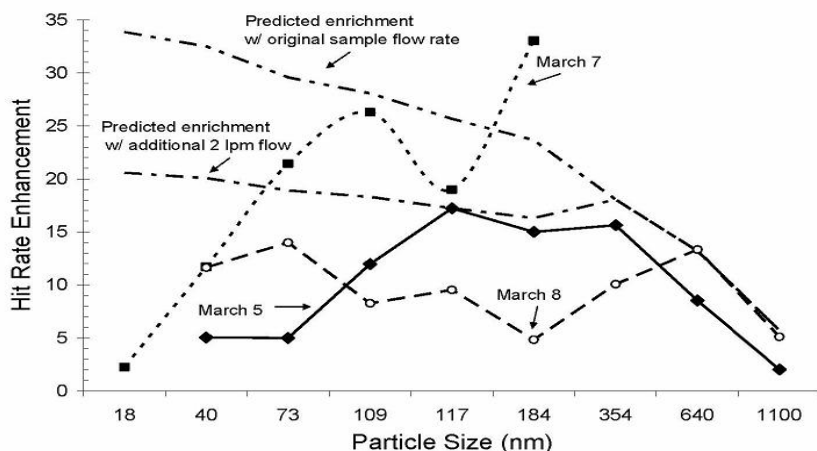


A field evaluation of the VACES concentrator coupled to the RSMS-3 ultrafine single particle mass spectrometer was conducted at the Pittsburgh EPA Supersite in March 2002 to determine the hit rate increase and elucidate possible particle composition changes introduced by the concentrator, based on single particle mass spectra.

Selected Results

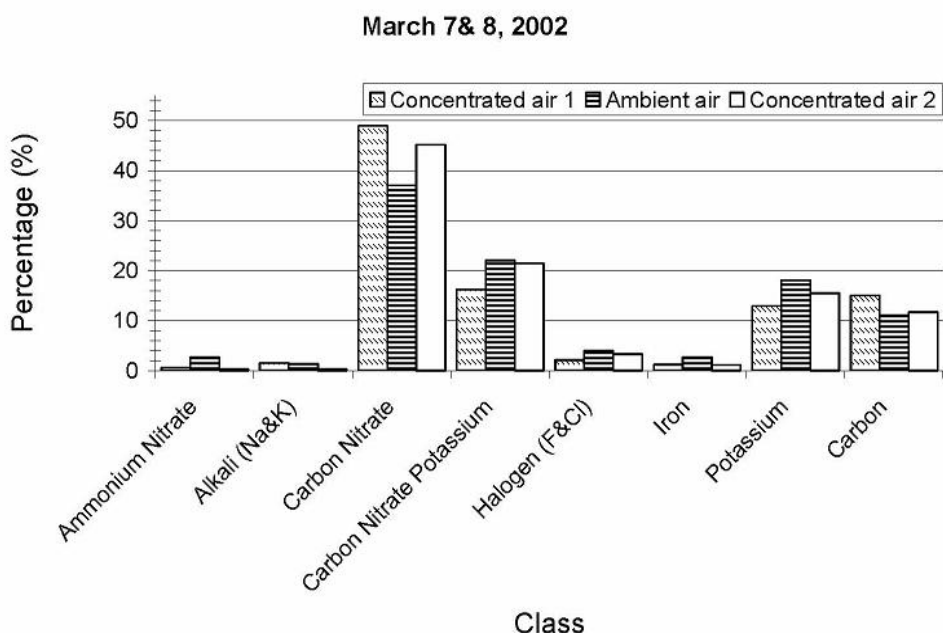
As shown in the below figure, the VACES was successful in increasing the hit-rates of the RSMS-3. The hit rate enhancement of RSMS-3 varies with particle size for a number of reasons. Since the VACES minor flow rate changed when RSMS-3 was sampling different particle sizes, while its major flow rate was fixed, the ratio of total-to-minor flow rate, and therefore the VACES concentration enrichment, changed with particle sizes, which is consistent with the predicted enrichment of particle concentration by VACES at large particle sizes and can readily be seen in the figure. With the VACES concentrator, particle hit rates of the RSMS-3 were increased by 10-17 times for the particles with sizes ranging from 109 to 354 nm. From size 640 nm to 1100 nm, the hit rate enhancements became smaller as the RSMS-3 sampling flow rate, and therefore the minor flow rate of the concentrator, increased. For the particles of 1100 nm, the enhancement of hit rates was only 2. The predicted enrichment was 5 at this point. The flow rate at this particle size was greater than 15 lpm, which plus the 3 lpm of dryer flow was too high for the VACES concentrator to operate in its optimum range [Sioutas et al., 1999]. At the small particle side, the hit rate enhancements also decreased as the flow rate decreased which is contrary to the predicted particle concentration enrichment that increased. At these small particle sizes, the flow rates (about 3 lpm) into RSMS-3 were lower than the design conditions for the concentrator, so particle losses to the walls of the diffusion dryer would be substantial. On the other hand, the enrichment of particle concentration by VACES is affected to a large extent by the actual minor flow ratio and deviates from its ideal value as this ratio becomes smaller (i.e., less than about 5%). This is because as this minor flow decreases, particle losses mostly on the collection nozzle of the virtual impactor increase, thereby decreasing the overall enrichment [Marple et al., 1980, Sioutas et al., 1994]. This is the case also with the virtual impactors used in the VACES to concentrate the grown ultrafine particles [Sioutas et al., 1999]. Despite these losses, the hit rate enhancements at 40 and 73 nm were about 5. Accuracy of the real flow rate measurement is another factor in difference between the predicted VACES concentration

enrichment and RSMS-3 hit rate enhancement. The ablation ability of RSMS-3 for different particle sizes [Kane and Johnston, 2000] would be another cause for the difference. It should be emphasized that this experiment was conducted with the RSMS-3 and VACES in their original configurations and the main premise of this research was to find out problems in coupling the two instruments together and ways to fix them, but no efforts were made to achieve the maximum enhancement of RSMS-3 hit rates.



During the three days of measurements, most of the particles were a mixture of carbonaceous material and ammonium nitrate with a variation across the spectrum from particles that were mostly carbonaceous to particles that were mostly ammonium nitrate. Both ambient and concentrated carbonaceous and ammonium nitrate composition distributions were indistinguishable with RSMS-3 suggesting that VACES does not introduce a significant artifact for those particles. Class comparisons between samples collected with and without the concentrator on March 7 and 8 are shown in the figure below. The four major classes were carbon nitrate, carbon nitrate potassium, potassium, and carbon. Particles in the ammonium nitrate class were not observed on these days. The experiments of March 7 and 8 were designed to sample concentrated particles immediately before and after ambient particles to identify whether or not a shift in particle composition occurred during the sampling period. There is a 4% difference in the particle fractions between the two concentrated samples that could be due to either change in ambient air or instrument drift. A 10% difference is also seen in the carbon nitrate class between the ambient air and the average of the two concentrated samples indicating a possible class shift from other nitrate containing classes to carbon nitrate. However, it was shown that this class shift was an artifact of the particle classification system, and that any

apparent class shift from ammonium to carbon nitrate was not due to the particle concentrator.



References

- Bein, K.J., Y. Zhao, A.S. Wexler, and M.V. Johnston (2004), *J. Geophys. Res.*, Submitted
- Kane, D.B. and M.V. Johnston (2000), *Environmental Science and Technology*, 34, 4887-4893.
- Kim, S., P. Jaques, M.C. Chang, J.R. Froines, and C. Sioutas (2001a), *J. Aerosol Sci.*, 32, 1281-1297.
- Kim, S., P. Jaques, M.C. Chang, C. Xiong, S.K. Friedlander, and C. Sioutas (2001b), *J. Aerosol Sci.*, 32, 1299-1314.
- Middha, P. and A.S. Wexler (2003), *Aerosol Sci. &Tech.*, 37, 907-915.
- Phares, D.J., K.P. Rhoads, and A.S. Wexler (2002), *Aerosol Sci. & Tech.*, 36, 583-592.
- Phares, D.J., K.P. Rhoads, M.V. Johnston, and A.S. Wexler (2003), *J. Geophys. Res.*, 108(D7), 8420.
- Rhoads, K.P., D.J. Phares, A.S. Wexler, and M.V. Johnston (2003), *J. Geophys. Res.*, 108(D7), 8418.
- Sioutas, C., S. Kim, and M.C. Chang (1999), *J. Aerosol Sci.*, 30, 1001-1017.

6. In-situ concentration of semi-volatile aerosol using water-condensation technology

In collaboration with investigators from the Carnegie Mellon University Supersite, we investigated the effect of concentrating semi-volatile aerosols using a water-condensation technology (Versatile Aerosol Concentration Enrichment System, VACES) and the Aerodyne Aerosol Mass Spectrometer (AMS) during measurements of ambient aerosol in Pittsburgh, PA.

The operation principle of the VACES is similar to that of other particle concentrators, but differs in that particles are grown by water condensation prior to passage through the virtual impactor. The instrument creates a super-saturation of water vapor by passing the air first through a warm saturator and then through a cold condenser. The super-saturation causes water condensation onto the particles, which as a result grow in size and can be concentrated without the need of a high pressure drop. The VACES was demonstrated to be capable of enriching the concentration of particles in the range of 0.01- 10 μm by a factor of up to 40 [Kim *et al.*, 2001a; Kim *et al.*, 2001b]. Its small size and modular design makes it well suited for studies using mobile exposure platforms. In addition, the VACES can be readily adapted to accommodate higher output flow rates, which are desirable in conducting human exposure studies.

Water condensation and a change in temperature of the air during the passage through the concentrator raises concerns of a possible change in gas / aerosol partitioning, i.e. sampling artifacts. However, a study by Zhao *et al.* [2004] found no detectable sampling artifacts. Here we describe our observations during field measurements in which the VACES concentrator was coupled to the Aerodyne Aerosol Mass Spectrometer (AMS) [Jayne *et al.*, 2000; Jimenez *et al.*, 2003]. The measurements were conducted during the Pittsburgh Air Quality Study at the central monitoring site in Pittsburgh, PA, during September 2002. The main aim of this study was to determine the applicability of the VACES-AMS combination to measurements of aerosol chemical composition during nucleation events. Because of the different nature of the problem, namely the very low aerosol concentrations during these events, attention has been given to small changes in aerosol composition (of the order of 5% of the concentrated mass) that were not relevant to the previous characterization studies of the VACES [Geller *et al.*, 2002; Kim *et al.*, 2001b; Misra *et al.*, 2004].

METHODS

VACES

The VACES concentrator is described in detail elsewhere [Kim *et al.*, 2001a; Kim *et al.*, 2001b]. The concentrator used in our studies consisted of a single sampling line operating at an intake flow rate of 112 liters per minute (LPM), which was checked before and after experiments using a gas flow meter.

Aerodyne AMS

The Aerodyne Aerosol Mass Spectrometer (AMS) measures size-resolved mass distributions and total mass loadings of non-refractory chemical species in/on submicron particles. This instrument and the associated quantification procedures have been described in detail in other publications

[Alfarra et al., 2004; Allan et al., 2004; Jayne et al., 2000; Jimenez et al., 2003], and only a brief summary will be given here. The results from the deployment of this instrument in Pittsburgh are described in Zhang et al.[2004a, b].

Experimental set-up

The VACES-AMS measurements were carried out on 10, 18, and 19 September 2002 at the central monitoring site of the Pittsburgh Air Quality Study [Wittig et al., 2004]. The site was located in an urban park, approximately 6 km from the downtown Pittsburgh.

The performance of the concentrator was assessed by performing several back-to-back tests during which the AMS was alternately used with and without the concentrator at its inlet.. Each run was about 20 – 40 min, long, half with the concentrator and half without it. The integrated concentrations of sulfate, nitrate, ammonium and organics, as well as their size distributions during the runs with the concentrator were compared with those during the runs without the concentrator. When the AMS was sampling behind the concentrator, its sampling inlet was connected to the minor flow of the virtual impactor via a silica-gel diffusion drier. The sampling flow of the AMS was the nominal 0.085 l min^{-1} , the rest of the minor flow ($\sim 4.9 \text{ l min}^{-1}$) was drawn by a separate vacuum pump. The concentration factor of the VACES was monitored regularly by attaching a TSI CPC3022 particle counter to the minor flow of the concentrator and comparing the counts with the counts without the concentrator. In parallel to the measurements with the AMS, the ambient aerosol size distributions in the size range from 10 nm to $2.5 \mu\text{m}$ in diameter were continuously monitored with two TSI SMPS systems (TSI 3936N25 and TSI 3936L10, TSI Inc.) and an APS system (TSI 3320, TSI Inc.).

RESULTS AND DISCUSSION

Effect of concentrator on semi-volatile aerosol material

The concentrations of PM sulfate, nitrate, ammonium, and organics measured during the experiments, as well as the corresponding concentration factors are given in Table 1. The increased concentration factors for nitrate, organics, and ammonium indicate that some extra material has been formed in the concentrator. The amount of the extra material (artifact) was calculated using the following formula:

$$\Delta C = \frac{C - C_a X}{X} \quad (1)$$

in which ΔC is the concentration of the substance that has formed in the concentrator; C and C_a are the concentrations measured with and without the concentrator, respectively; X is the actual (or true) concentration factor taken to be that of sulfate, which is the least likely subjected to the condensation artifacts (due to the very low vapor pressure of sulfuric acid). The calculated artifacts are given in Table 2. The Table also contains relative magnitude of the artifacts: relatively to the original concentration of the species as well as relatively to the total ($\text{PM}_{2.5}$) aerosol mass. It is clear that even though the relative magnitude of the artifact may be large, its

absolute value is small. For example, for the three days of the study the average nitrate artifact was found to be 131%, 159%, and 21% of the original nitrate concentration. However, the corresponding average absolute artifact concentrations are 0.55, 1.0, and 0.04 $\mu\text{g}/\text{m}^3$. Because of the low absolute values of the artifact, its contribution to the total aerosol mass is insignificant (less than 3% for nitrate).

Size dependence of the artifact

Figure 1 shows size distributions of the measured chemical species during the three experiments. The size distributions during the VACES runs were scaled by the concentration factors of sulfate for each of the runs. The size distributions of sulfate are preserved after the passage through the concentrator, while that of nitrate, and to a lesser degree those of ammonium and organics, are not, except for the run of 19 September. The striking feature on 10 and 18 September is the increase of nitrate concentration at small sizes, in the size range of 100 - 200 nm. Similarly, on these days the enhancement factor for the integrated sulfate concentration is smaller than the factor for nitrate (Table 1). The change of size distribution of nitrate, together with its concentration factor that is higher than that of sulfate, suggests formation of nitrate in VACES on 10 and 18 September. The changes in the size distributions of nitrate on Sept. 10 and 18 are far larger than the uncertainties on the AMS measurement. As Figure 1 shows, the extra nitrate (as well as some organics) was mostly formed at small sizes (smaller than about 300 nm), while the shape of the distribution was mostly preserved at and around the mode of the mass distribution (500 – 700 nm). The probable reason for such behavior is the shape of the size distribution of the aerosol surface area. Condensation of the gas-phase species will proceed mostly to the size range of maximum surface area. The average surface area size distributions of ambient aerosol during the experiments, as measured with the SMPS, are shown in Fig. 2. The maximum of the surface area distribution is located at sizes smaller than the mode of the volume (mass distribution), which explains why the extra nitrate was forming mostly at small sizes.

Recommendations

Given the potential of artifact formation in the concentrators using water-condensation technology it is recommended to use a denuder to remove interfering species from the air stream prior to its entrance into the humidifier. This, however, may lead to particle losses in the ultra-fine size range. Even though no artifact formation was observed on the cleanest day of the study (19 September), care should be taken when using VACES for nucleation and new particle growth studies, since even a small artifact can be large compared to the very small mass of these particles. For the exposure studies we would recommend to monitor concentration of species before and after the concentrator such that concentration factors for each compound are known. These individual concentration factors can be then used to assess health effects (or lack thereof) of each compound. We would also like to reiterate, that the observed artifact formation is small in comparison to the total mass concentration of the concentrated aerosol.

SUMMARY AND CONCLUSIONS

The effect of water condensation on semi-volatile aerosol species during their passage through a particle concentrator was assessed using the VACES concentrator coupled to the Aerodyne Aerosol Mass Spectrometer during measurements of ambient aerosol, with the following conclusions:

- The size distribution of sulfate is preserved after passage through the concentrator at all conditions encountered during the study.
- The size distributions of ammonium, organics and nitrate are preserved at relatively clean conditions (sulfate concentrations around $7 \mu\text{g}/\text{m}^3$), while under more polluted conditions (sulfate concentrations around $20 \mu\text{g}/\text{m}^3$) they exhibit an increase at small sizes (100-200 nm in vacuum aerodynamic diameter, or approximately 150-300 nm in physical diameter). Such an increase is especially pronounced for nitrate.
- The increase of nitrate and organic concentrations at small sizes after the passage through the concentrator corresponds to the region of the maximum aerosol surface area and fastest gas-to-particle transfer.
- The absolute increase in concentration of nitrate observed in this study is rather small, of the order of $1 \mu\text{g}/\text{m}^3$ or less (i.e., 0.3 – 2.7 % of the total aerosol mass concentration) and can be neglected for many practical purposes.
- An analysis of thermodynamic processes in the concentrator indicates that the formation of extra material in the concentrator is likely due to redistribution of the gas-phase material to the aerosol phase. The modeling indicates that nitrate artifact will be most pronounced in ammonia-limited conditions, while in ammonia-rich environment it becomes negligible.
- Even though the extent of the artifact is limited, to avoid its formation completely it is recommended to operate VACES with a denuder and / or with its condenser temperature set to be equal the ambient temperature. If no denuder is used, we recommend that concentration of individual compounds is measured both before and after concentrator, such that concentration factors for individual species are known.

A paper describing these result as well as modeling of the (small) artifacts during the concentration enrichment process has been submitted to the *Journal of Geophysical Research*. (Khlystov, A., Zhang, Q., Jimenez, J.L., Stanier, C.O., Pandis, S., Worsnop, D.R., Misra, C., Fine, P.M. and Sioutas, C. “On Concentrating Semi-volatile Aerosols Using Water-Based Condensation Technology” Submitted to *Journal of Geophysical Research*, April, 2004.)

REFERENCES

- Alfarra, M.R., H. Coe, J.D. Allan, K.N. Bower, H. Boudries, M.R. Canagaratna, J.L. Jimenez, J.T. Jayne, A. Garforth, S.M. Li, and D.R. Worsnop, Characterization of Urban and Regional Organic Aerosols in the Lower Fraser Valley Using Two Aerodyne Aerosol Mass Spectrometers, *Atmospheric Environment*, *In press*, 2004.
- Allan, J.D., K.N. Bower, H. Coe, H. Boudries, J.T. Jayne, M.R. Canagaratna, D.B. Millet, A.H. Goldstein, P.K. Quinn, R.J. Weber, and D.R. Worsnop, Submicron aerosol composition at Trinidad Head, CA during ITCT 2K2, its relationship with gas phase volatile organic

- carbon and assessment of instrument performance., *Journal of Geophysical Research - Atmospheres*, *In press*, 2004.
- Allan, J.D., J.L. Jimenez, P.I. Williams, M.R. Alfarra, K.N. Bower, J.T. Jayne, H. Coe, and D.R. Worsnop, Quantitative sampling using an Aerodyne aerosol mass spectrometer: 1. Techniques of data interpretation and error analysis (vol 108, art no 4090, 2003), *Journal of Geophysical Research-Atmospheres*, 108 (D9), -, 2003.
- Ansari, A.S., and S.N. Pandis, Prediction of multicomponent inorganic atmospheric aerosol behavior, *Atmospheric Environment*, 33 (5), 745-757, 1999.
- Eatough, D.J., Y.B. Pang, and N.L. Eatough, Determination of PM_{2.5} sulfate and nitrate with a PC-BOSS designed for routine sampling for semi-volatile particulate matter, *Journal of the Air & Waste Management Association*, 49, 69-75, 1999.
- Geller, M.D., S. Kim, C. Misra, C. Sioutas, B.A. Olson, and V.A. Marple, A methodology for measuring size-dependent chemical composition of ultrafine particles, *Aerosol Science and Technology*, 36 (6), 748-762, 2002.
- Jayne, J.T., D.C. Leard, X.F. Zhang, P. Davidovits, K.A. Smith, C.E. Kolb, and D.R. Worsnop, Development of an aerosol mass spectrometer for size and composition analysis of submicron particles, *Aerosol Science and Technology*, 33 (1-2), 49-70, 2000.
- Jimenez, J.L., J.T. Jayne, Q. Shi, C.E. Kolb, D.R. Worsnop, I. Yourshaw, J.H. Seinfeld, R.C. Flagan, X.F. Zhang, K.A. Smith, J.W. Morris, and P. Davidovits, Ambient aerosol sampling using the Aerodyne Aerosol Mass Spectrometer, *Journal of Geophysical Research-Atmospheres*, 108 (D7), -, 2003.
- Kim, S., P.A. Jaques, M.C. Chang, T. Barone, C. Xiong, S.K. Friedlander, and C. Sioutas, Versatile aerosol concentration enrichment system (VACES) for simultaneous in vivo and in vitro evaluation of toxic effects of ultrafine, fine and coarse ambient particles - Part II: Field evaluation, *Journal of Aerosol Science*, 32 (11), 1299-1314, 2001a.
- Kim, S., P.A. Jaques, M.C. Chang, J.R. Froines, and C. Sioutas, Versatile aerosol concentration enrichment system (VACES) for simultaneous in vivo and in vitro evaluation of toxic effects of ultrafine, fine and coarse ambient particles - Part I: Development and laboratory characterization, *Journal of Aerosol Science*, 32 (11), 1281-1297, 2001b.
- Misra, C., P.M. Fine, M. Singh, and C. Sioutas, Development and evaluation of a compact facility for exposing humans to concentrated ambient ultrafine particles, *Aerosol Science and Technology*, 38 (1), 27-35, 2004.
- Pankow, J.F., An Absorption-Model of Gas-Particle Partitioning of Organic-Compounds in the Atmosphere, *Atmospheric Environment*, 28 (2), 185-188, 1994.
- Peters, A., D.W. Dockery, J. Heinrich, and H.E. Wichmann, Short-term effects of particulate air pollution on respiratory morbidity in asthmatic children, *European Respiratory Journal*, 10 (4), 872-879, 1997.
- Pope, C.A., D.W. Dockery, and J. Schwartz, Review of Epidemiological Evidence of Health-Effects of Particulate Air-Pollution, *Inhalation Toxicology*, 7 (1), 1-18, 1995.
- Sioutas, C., S. Kim, and M. Chang, Development and evaluation of a prototype ultrafine particle concentrator, *Journal of Aerosol Science*, 30 (8), 1001-1017, 1999.
- Thurston, G.D., K. Ito, C.G. Hayes, D.V. Bates, and M. Lippmann, Respiratory Hospital Admissions and Summertime Haze Air-Pollution in Toronto, Ontario - Consideration of the Role of Acid Aerosols, *Environmental Research*, 65 (2), 271-290, 1994.
- Willeke, K., and P.A. Baron, *Aerosol measurement : principles, techniques, and applications*, 876 pp., Van Nostrand Reinhold, New York, 1993.

- Wittig, A.E., N. Anderson, A.Y. Khlystov, S.N. Pandis, C. Davidson, and A.L. Robinson, Pittsburgh Air Quality Study overview and preliminary scientific findings, *Atmospheric Environment*, *in press*, 2004.
- Zhang, Q., M.C. Canagaratna, J.T. Jayne, D.R. Worsnop, and J.L. Jimenez, Size-Resolved Chemical Composition and Temporal Variation of Submicron Particles in Pittsburgh - Implications on Aerosol Sources and Processes., *Journal of Geophysical Research-Atmospheres*, *Submitted for publication*, 2004a.
- Zhang, Q., C.O. Stanier, M.C. Canagaratna, J.T. Jayne, D.R. Worsnop, S.N. Pandis, and J.L. Jimenez, Insights into the Chemistry of Nucleation Bursts and New Particle Growth Events in Pittsburgh Based on Aerosol Mass Spectrometry, *Environmental Science and Technology*, *Submitted for publication*, 2004b.
- Zhao, Y., K.J. Bein, A.S. Wexler, C. Misra, P.M. Fine, and C. Sioutas Using a Particle Concentrator to Increase the Hit Rates of Single Particle Mass Spectrometers., *Journal of Geophysical Research-Atmospheres*, *Submitted for publication*, 2004.

Table 1. Average concentrations and standard deviations in $\mu\text{g}/\text{m}^3$ of the measured aerosol components and the corresponding concentration factors.

Date	Sulfate			Ammonium			Nitrate			Organics		
	OFF ¹	ON ²	F ³	OFF	ON	F	OFF	ON	F	OFF	ON	F
10/9/02	19.3 ±0.9	201 ±3.1	10.4 ±0.5	4.8 ±0.5	61.3 ±1.7	12.7 ±1.3	0.4 ±0.1	10.0 ±0.3	24.1 ±3.3	5.8 ±0.2	60.5 ±0.7	10.4 ±0.4
18/9/02	21.3 ±1.0	278 ±3.6	13.1 ±0.6	7.3 ±0.6	95.3 ±2.1	13.0 ±1.1	0.6 ±0.1	21.3 ±0.4	33.9 ±3.8	7.6 ±0.2	122 ±1.0	16.1 ±0.5
19/9/02	6.6 ±0.6	143 ±2.6	21.8 ±1.9	2.4 ±0.3	50.7 ±1.5	21.5 ±3.1	0.2 ±0.0	5.2 ±0.2	26.4 ±5.3	2.9 ±0.1	68.9 ±0.7	24.0 ±1.3

¹OFF: when the concentrator was off

²ON: when the concentrator was on;

³F: the concentration factor;

Table 2. Average concentrations of the extra ammonium, nitrate and organics formed in the concentrator (see Equation 1), their fractions of the original concentration of each of the species (dC/C_a), and their fractions of the total aerosol mass (dC/M). Standard deviations of each value are also given

Date	Ammonium			Nitrate			Organics		
	dC , $\mu\text{g}/\text{m}^3$	dC/C_a , %	dC/M , %	dC , $\mu\text{g}/\text{m}^3$	dC_a/C , %	dC/M , %	dC , $\mu\text{g}/\text{m}^3$	dC_a/C , %	dC/M , %
10/9/02	1.05 ± 0.6	21.7 ± 12.3	3.5 ± 1.9	0.55 ± 0.1	131 ± 26	1.8 ± 0.3	-0.01 ± 0.4	-0.1 ± 6.4	0.0 ± 1.2
18/9/02	-0.01 ± 0.7	-0.2 ± 1.4	0.0 ± 0.2	1.0 ± 0.1	159 ± 25	2.7 ± 0.3	1.75 ± 0.5	23.1 ± 6.8	4.8 ± 1.4
19/9/02	-0.04 ± 0.4	-1.6 ± 16	-0.3 ± 0.5	0.04 ± 0.0	20.9 ± 23	0.3 ± 0.4	0.29 ± 0.3	10.0 ± 10.8	2.4 ± 2.6

Figure 1. Size distributions of sulfate, ammonium, nitrate, and organics measured without and with the VACES concentrator (solid and broken lines, respectively). Measurements with the concentrator are plotted using the right-hand axes, which were scaled by the corresponding concentration factor of sulfate. Note the difference in scales for sulfate and nitrate.

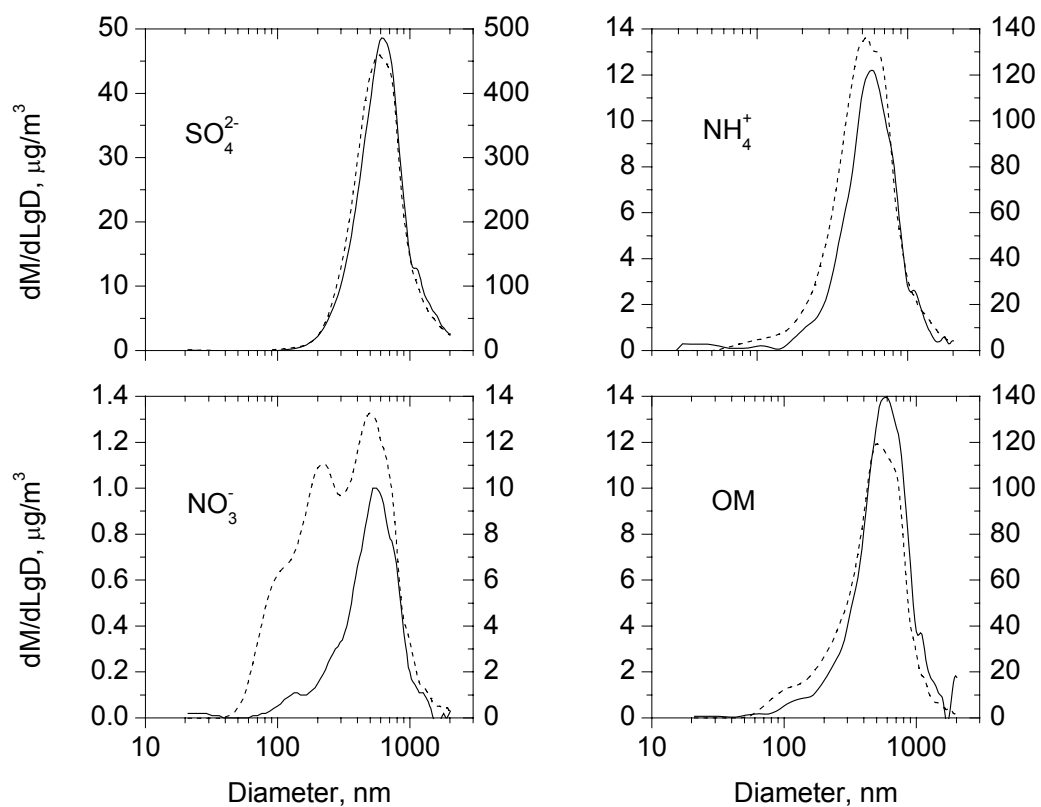


Figure 1A. September 10, 2002

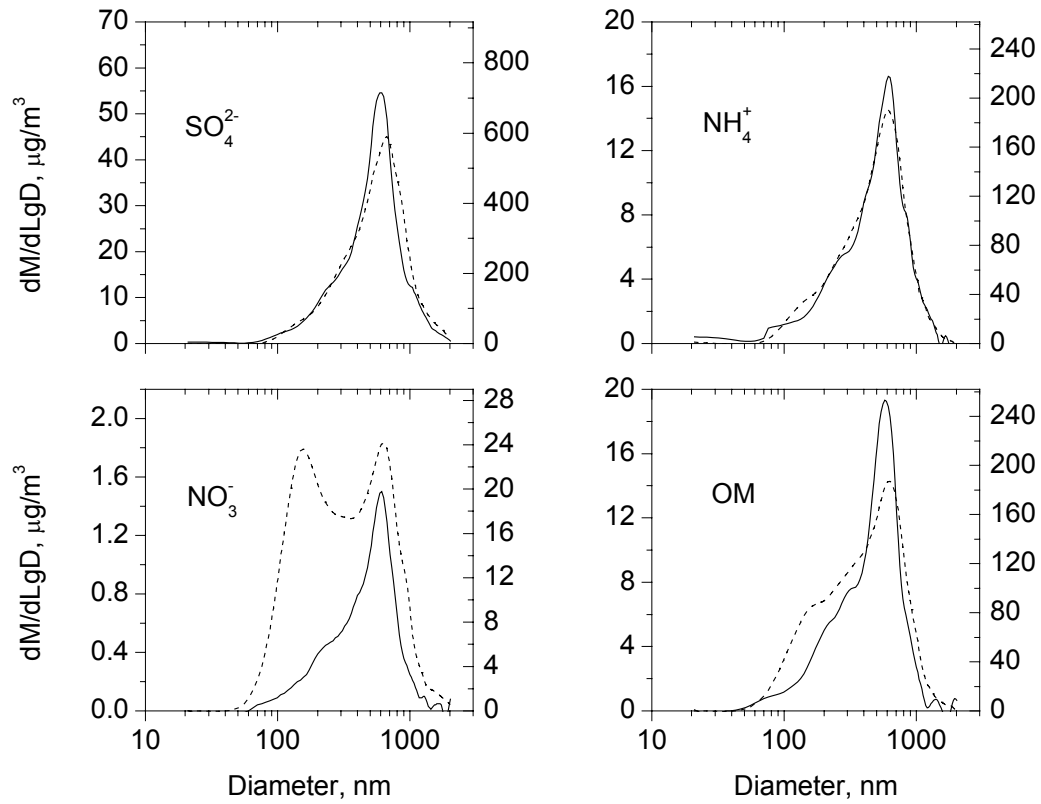


Figure 1B. September 18, 2002

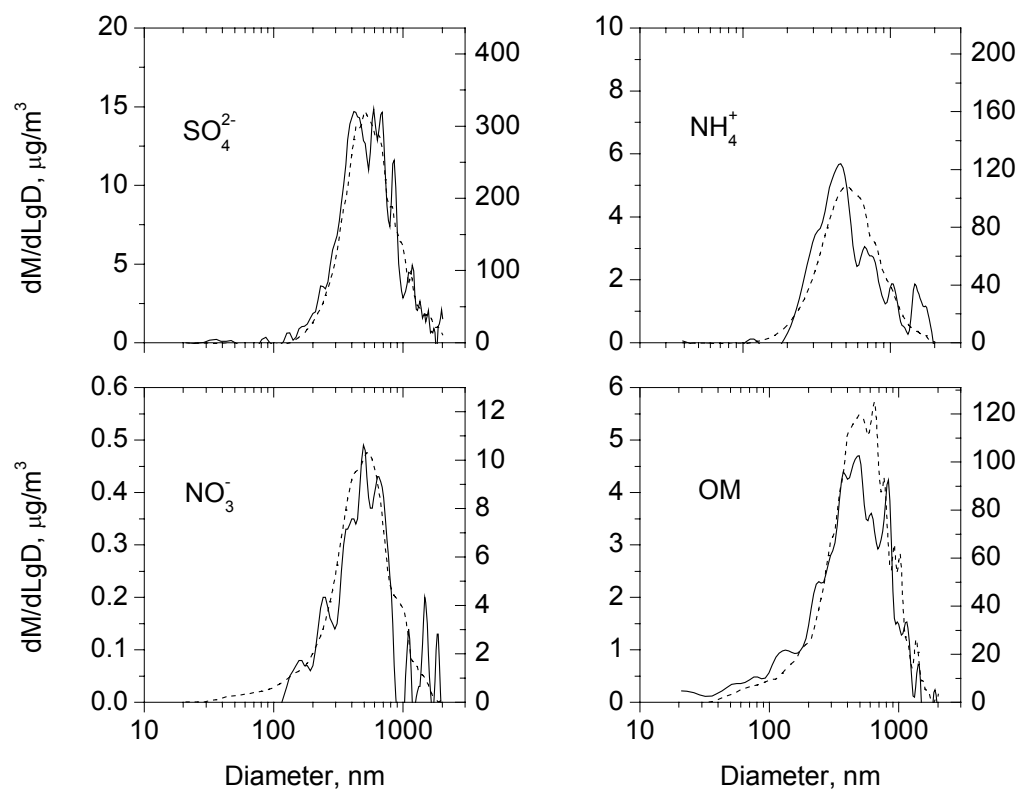
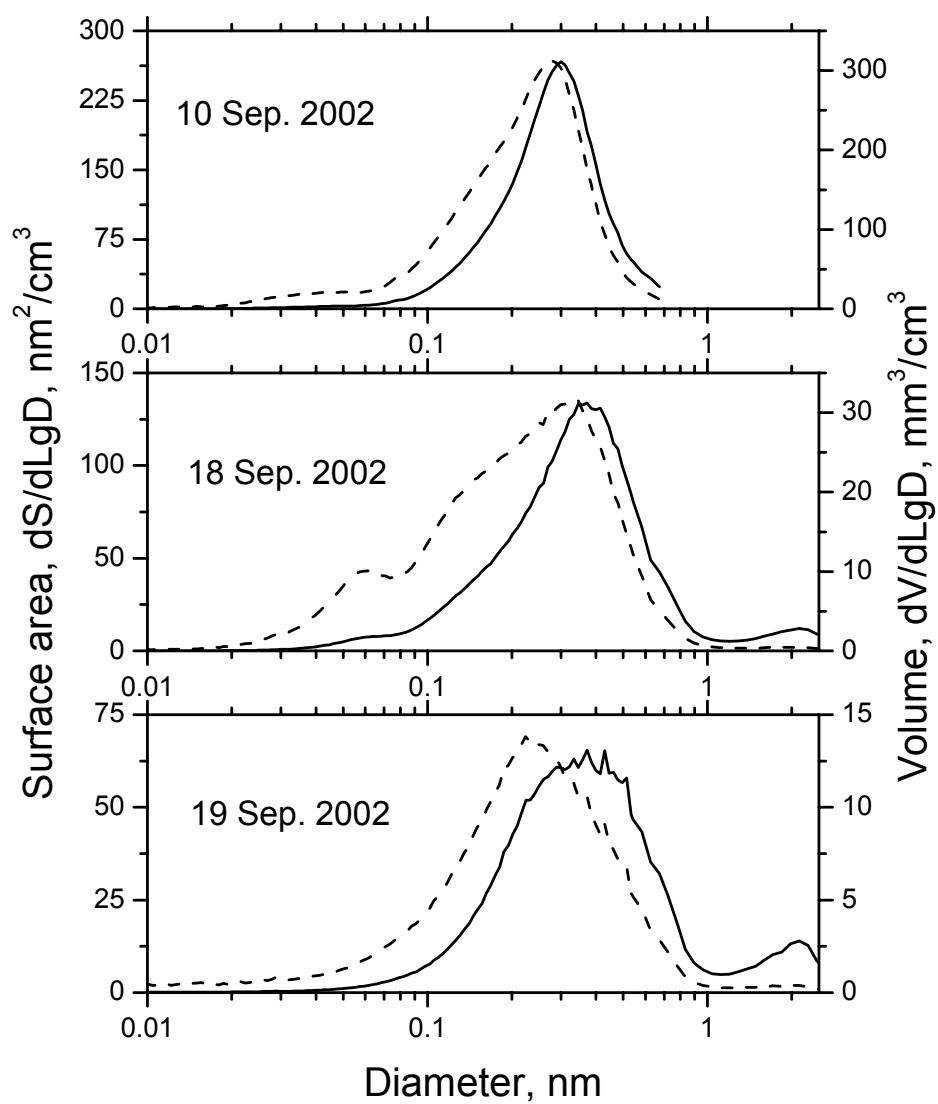


Figure 1C. September 19, 2002

Figure 2. Volume (solid lines) and surface area (broken lines) size distributions measured with the SMPS.



7. Chemical Characterization of Ultrafine Particles in the LA Basin

Background

Recent observations revealed that ultrafine particles (diameters less than 100 nm) are comparatively more toxic than larger particles with similar chemical composition and mass. Additional studies have demonstrated a dramatic drop of ultrafine number concentrations with increasing distance from busy freeways in the Los Angeles basin, demonstrating that vehicular pollution is the major source of ultrafine particles, and that high particle number can be a local phenomenon. Little is known about how the chemical constituents of ultrafine particles are distributed within the ultrafine size range. The objective of the current study is to give a more complete representation of size-fractionated ultrafine chemical characteristic by sampling across four different locations and multiple seasons in the Los Angeles Basin.

Methods

Fourteen-day composite size-fractionated PM_{2.5} samples, including several ultrafine size ranges, were collected at four sites and three seasons in the Los Angeles Basin. The seasons are defined as: fall 2002 (September – November); winter 2002 (December – February); and summer 2003 (June – August). The first site was at the University of Southern California near downtown Los Angeles. This sampling location is downwind of a major freeway and represents an urban mix of industrial, vehicular and construction sources. The Long Beach station is located on one of the busiest streets in Long Beach, and is located about one half a mile northeast of a major freeway. The Upland site is located in a residential area at least 3 miles away from a major freeway. The sampling location at Riverside is at the Citrus Research Center and Agricultural Experiment Station (CRS – AES), a part of the University of California – Riverside. Riverside is 90 km east of downtown Los Angeles and is primarily a residential and commercial center. Because of the relatively western location and the surrounding urban environment, Long Beach and USC are considered “source” sites where fresh particles are emitted primarily from vehicular and industrial sources. The other sites, Riverside and Upland are designated “receptor” sites where the aerosol is composed of advected, aged and photochemically processed air masses from the central Los Angeles area. The transport time of air masses from source to receptor sites can vary from a few hours to more than a day. A NanoMOUDI (Nano-Micro orifice uniform deposit impactor, MSP Corporation, Minneapolis, MN) impactor collected samples continuously at 10 lpm for a period of two weeks at each site. The NanoMOUDI is a cascade impactor operating under low pressure connected to a MOUDI after the 56 nm cut-point stage and includes three additional stages with cut points of 32nm, 18nm and 10 nm (Marple and Olson, 1999). Measurements of size-fractionated mass, inorganic ions (Sulfate and nitrate), and elemental and organic carbon (EC/OC) were performed on all MOUDI and NanoMOUDI aluminum foil substrate samples

Results and Discussion

In the last report the PM_{0.18} mass and the chemical species in the ultrafine range (diameters less than 180 nm) measured at the source and receptor sites for different seasons were presented. Further, the report also showed the size distributions of the chemical composition measured at

different sites for all the three seasons. In addition to the NanoMOUDI measurements, a collocated SMPS and several gas pollutant monitors were deployed at selected sites and seasons over the same two-week period that the NanoMOUDI was sampling. Analysis of the size distributions measured by SMPS and NanoMOUDI/MOUDI appeared to be quite similar for all sites and various seasons and the relative similarity in the distributions measured by the two instruments increased our confidence in using the SMPS as the source of continuous particle size distribution data for further analysis.

Figures 1 through 4 display the diurnal variations of particle number and gaseous pollutant concentrations averaged by time of day over the two weeks of NanoMOUDI sampling. The diurnal trends of PN in different size ranges and gaseous pollutants at USC during the winter sampling period are shown in Figures 1a and b. USC is near a freeway and traffic is expected to be the primary source of particles at this site. The mass size distribution from the earlier report has already been shown to be driven by OC, and the EC levels were found to be highest in fall and winter. The diurnal patterns of CO and NO_x, which are also emitted directly from vehicles, are very similar to the diurnal patterns of particle number concentrations. The morning peak of these pollutants corresponds to the morning commute. The similarities in the diurnal trends are most striking for particles less than 100 nm in diameter, which are the size ranges of particles generated by traffic. The correspondence between particle numbers in these size ranges and co-pollutant gaseous emissions suggest that traffic is the major contributor to ultrafine PM at USC during the winter. The hourly number concentrations of ultrafine particles in the 56 – 180 nm size ranges were well correlated with CO and NO_x, with Pearson correlation coefficients (*r*) ranging from 0.65 to 0.78 (Table 1).

Figures 2a and b show similar data from the fall sampling period in Riverside, where, pollutants advected from upwind sources combine with local emissions. The EC concentrations at Riverside were relatively high during this time period, suggesting significant diesel engine contributions. The diurnal patterns of CO and NO_x in Figure 2b, which follow one another very closely, are very similar to that of the PN size ranges in Figure 2a. Similar to USC in the winter, vehicular emissions are a major contributor to particle number concentrations in fall at Riverside.

Figures 3a and b show the average diurnal trends of PN and these co-pollutants gases at Long Beach during the summer. The most interesting observation at this site is the similarity of diurnal patterns between particle numbers in the smaller size fractions (less than 56 nm) and O₃. The same trend is also observed for PN vs. O₃ Pearson correlation coefficients in Table 1. The *r*-values for the smaller particles are significantly high with *r*'s equal to 0.64 and 0.69 for particles in the size ranges 0-32 and 32-56 nm respectively. In addition to primary emissions, photochemical reactions in the atmosphere can form new particles via nucleation or form new particle mass by condensation of low volatility reaction products onto existing particle surfaces. It is expected that nucleation is more likely to occur during the summer with elevated photochemical activity due to larger solar zenith angles. The same conditions also favor photochemical ozone production. The similarity in diurnal patterns of particle numbers in the 18-32 nm and 32-56 nm ranges and O₃ observed for this period suggest a photochemical origin for these particles. Studies have showed that nucleation can form particles in the size range of 1-2 nm, which can subsequently grow to the 30-50 nm range by condensation of low volatility organics on these nuclei.

To confirm this observation, plots of particle number concentrations for different ultrafine PM ranges and gaseous pollutants at USC during the summer are given in Figures 4a and b

respectively. Again, similarities in the patterns between the smaller particle ranges and ozone, which were not observed in the winter (Figure 1), suggest that the formation processes of both may depend on photochemical activity levels. Figures 3 and 4 also reveal that vehicular emissions are still a major source of ultrafine particles in the summer, as evident from the increase in the concentrations of most size ranges during the morning commute hours (i.e., between 6AM and 9AM).

Table 1 shows Pearson correlation coefficients (r) between the size-fractionated particle number counts and gaseous pollutant concentrations over the same two weeks of data plotted in Figures 1 through 4. Also included is additional data from the fall sampling period at Long Beach. During fall and winter periods, where vehicular emissions become the dominant source of ultrafine PM, the larger particles (greater than 56nm in diameter) are correlated well with CO and NO_x (r greater than 0.6 in most of the cases), while very low correlations are observed between O₃ and PN of any size range. In our study, the traffic dominated sites, such as USC in winter and Riverside in fall, demonstrated similarly high correlations between PN and co pollutant gases like CO and NO_x. The diversity of particle sources in the summer period (i.e., vehicles and secondary formation) in both Long Beach and USC results in a decrease of the hourly correlation coefficients of PN vs. CO and NO_x, while the correlation between PN and O₃ increases to moderately high levels (r of 0.54-0.69 for particles in sub 100 nm range). As discussed above, the moderate to high correlations between ultrafine particles (sub 56nm range) and O₃ during summer might be indicative of secondary organic aerosol formation, especially considering the similarity in the diurnal trends of the concentrations of these two species (Figures 1-4), and the organic carbon mode at these particle sizes observed in the summer with the NanoMOUDI (Figures for which were given in a previous report).

Table 1. Size fractionated PN vs. gas pollutants - Pearson correlation coefficients (r) at source and receptor sites

Size range (nm)	Fall Long Beach			Size range (nm)	Fall Riverside		
	CO	NO _x	O ₃		CO	NO _x	O ₃
0-32	-0.26	-0.03	0.26	0-32	0.48	0.66	-0.45
32-56	0.20	0.31	-0.15	32-56	0.67	0.84	-0.50
56-100	0.49	0.52	-0.38	56-100	0.78	0.80	-0.51
100-180	0.66	0.66	-0.50	100-180	0.75	0.60	-0.37
180-320	0.68	0.70	-0.47	180-320	0.69	0.46	-0.18
320-1000	0.48	0.56	-0.30	320-1000	0.59	0.32	-0.04

Size range (nm)	USC Winter			Size range (nm)	Summer Long Beach		
	CO	NO _x	O ₃		CO	NO _x	O ₃
0-32	0.09	0.23	-0.03	0-32	0.25	0.28	0.64
32-56	0.38	0.54	-0.10	32-56	0.22	0.24	0.69
56-100	0.65	0.78	-0.13	56-100	0.33	0.40	0.54
100-180	0.65	0.75	-0.05	100-180	0.46	0.63	0.40
180-320	0.64	0.62	-0.06	180-320	0.47	0.63	0.25
320-1000	0.53	0.45	0.01	320-1000	0.32	0.61	0.14

Size range (nm)	USC Summer		
	CO	NO _x	O ₃
0-32	0.25	0.28	0.62
32-56	0.16	0.16	0.68
56-100	0.19	0.21	0.59
100-180	0.35	0.41	0.44
180-320	0.26	0.31	0.39
320-1000	0.29	0.36	0.21

Figure 1. USC winter sampling period - diurnal trends

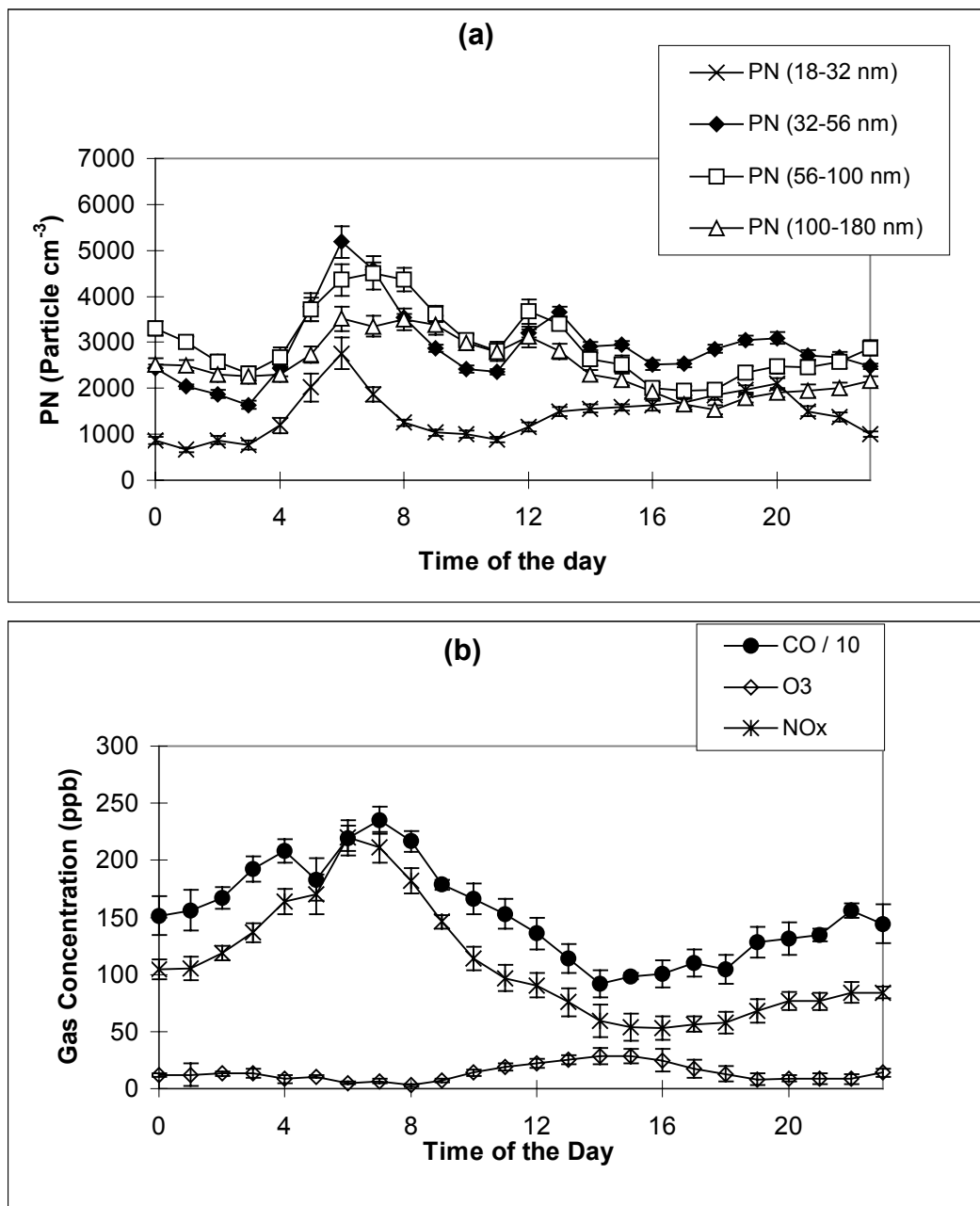


Figure 2. Riverside fall sampling period - diurnal trends

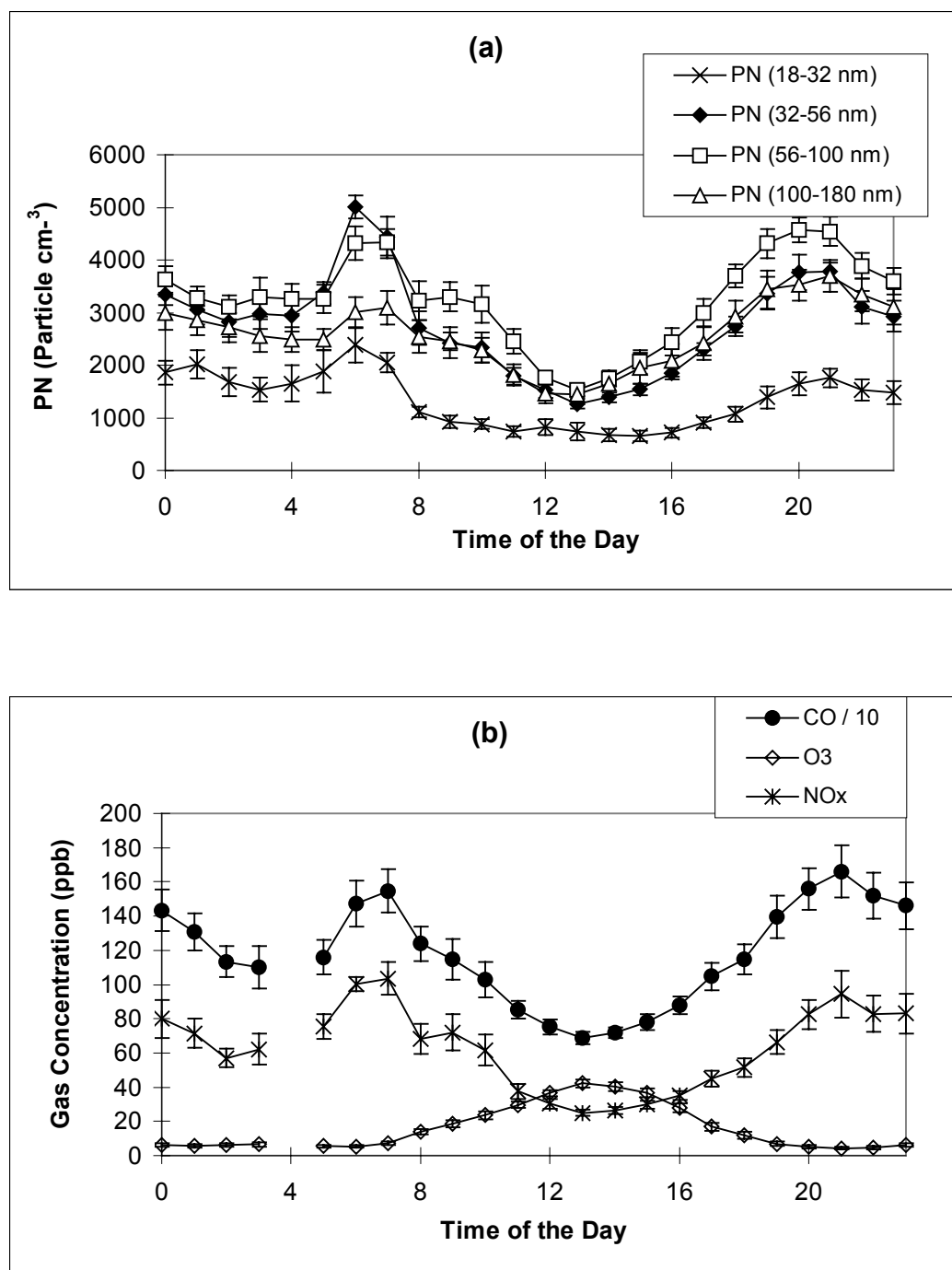


Figure 3. Long Beach summer sampling period - diurnal trends

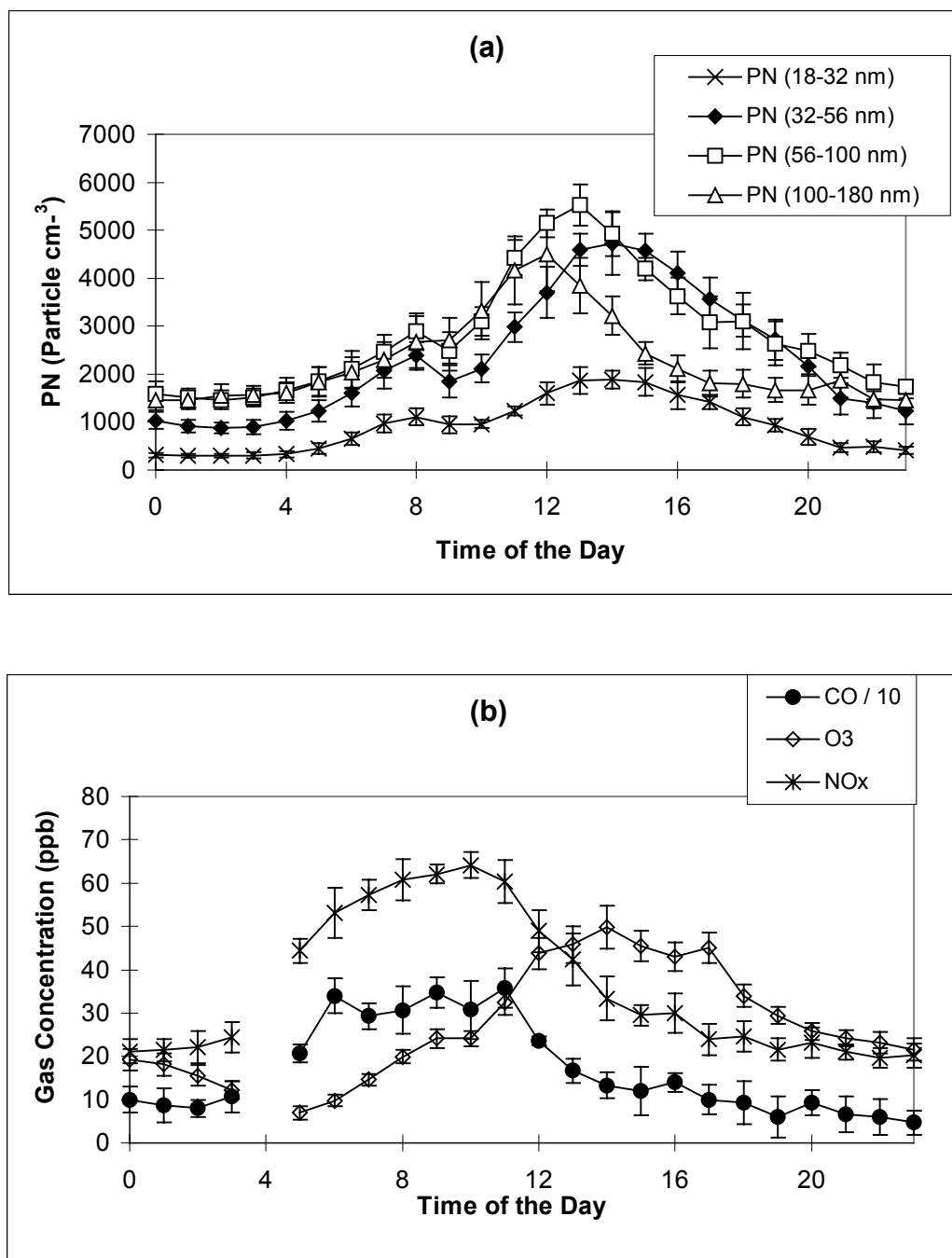
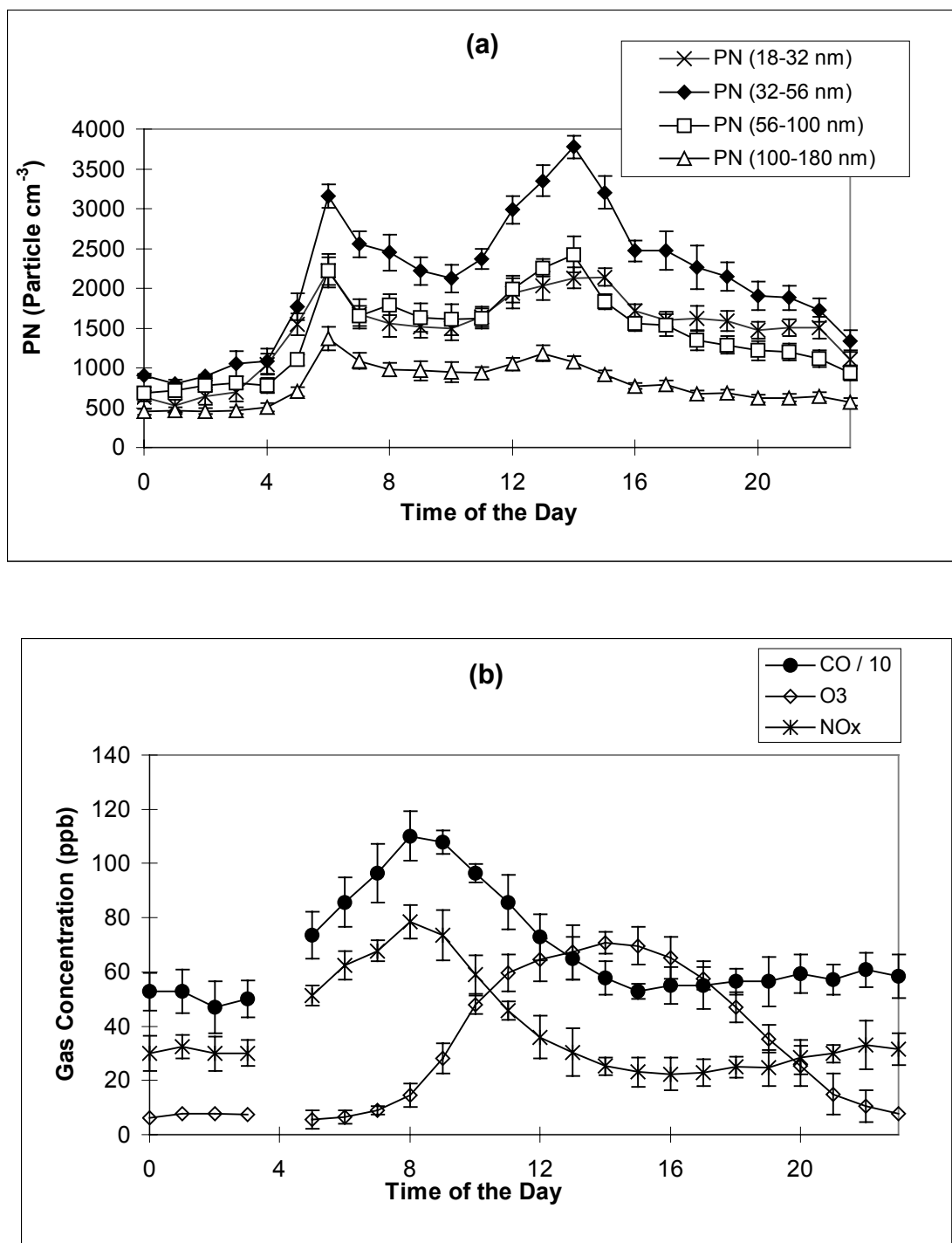


Figure 4. USC summer sampling period - diurnal trends



8. Penetration of freeway ultrafine particles into indoor environment

Previously we have reported high concentrations of ultrafine particles near major freeways (Zhu et al., 2002a; Zhu et al., 2002c). These results imply increased exposure to harmful pollutants in areas close to such hot spots. Many urban residences and business are located in close proximity to busy roadways. Consequently, indoor environments in urban areas may experience significant concentrations of outdoor ultrafine particles, exposing tenants to potentially toxic pollutants. People spend over 80% of their time indoors, therefore characterization of indoor ultrafine particles of outdoor origin and assessment of their penetration efficiencies are important factors in determining human exposure to outdoor contaminants. The present study determines penetration behavior of outdoor ultrafine particles into indoor environments in areas close to freeways. Results from this research have important implications concerning personal exposure to freeway related ultrafine particles and possible health consequences.

Four two-bedroom apartments in the vicinity of the I-405 Freeway in Los Angeles, CA were selected for this study. These apartments are in identical buildings with the same interior layouts. Three of the four apartments (Apt 1, 2 and 3) are on the eastern side of the 405 Freeway. These three apartments are on the third floor with windows 3 m above a sound barrier wall. The distances between apartments 1-3 and the wall range from 15 m to 40 m. All three apartments are separated by no more than 50 m. The fourth apartment (Apt 4) is on the opposite, western, side of the 405 Freeway, 15 m from the sound barrier wall. Apt 4 is on the second floor with windows 0.5 m above the wall. All the apartments are about 8 years old with central mechanical ventilation systems that can be turned on or off.

Both indoor and outdoor ultrafine particle size distributions in the size range of 6 to 220 nm were measured simultaneously by two Scanning Mobility Particle Sizers (SMPS). Sampling flow rates of the SMPSs were adjusted to 1.5 l/min, with a sheath flow of 15 l/min, to measure particles as small as 6 nm, and to minimize diffusion losses of ultrafine particles during sampling. Sampling flow was checked on site on a daily basis to ensure absence of flow leakage. Data reduction and analysis of the SMPS output were done by the Aerosol Instrument Manager software (version 4.0, TSI Inc., St. Paul., MN). Carbon monoxide (CO), carbon dioxide (CO₂) concentrations, ambient temperature, relative humidity and air exchange rates were also monitored during the measurement.

Figure 1 shows averaged particle size distributions and indoor/outdoor ratios for studied apartment 1. Figure 1(a) shows day time (10 am – 5 pm) and figure 1(b) illustrates night time indoor and outdoor particle size distributions, with the x- and y-axes indicating particle diameter (nm) and particle number concentration as $dN/d\log D_p$ (cm^{-3}), respectively. Each graph indicates the number of 3-minute observations averaged to obtain indoor and outdoor particle size distribution curves. Figure 1(c) shows size dependent indoor/outdoor ratios during day and night times. For this apartment, particle number concentrations were lower than those observed previously near the 405 freeway

(Zhu et al., 2002b). A sound barrier wall and condensed trees separating the freeway from sampling locations may have contributed to loss of particles to the wall. Sites used for this study were 5 miles south of the previous sampling site and measurements were performed from an elevation. The vertical profile may have contributed to lower number concentrations. Meteorological conditions, specifically higher wind speeds, also favored lower particle concentrations.

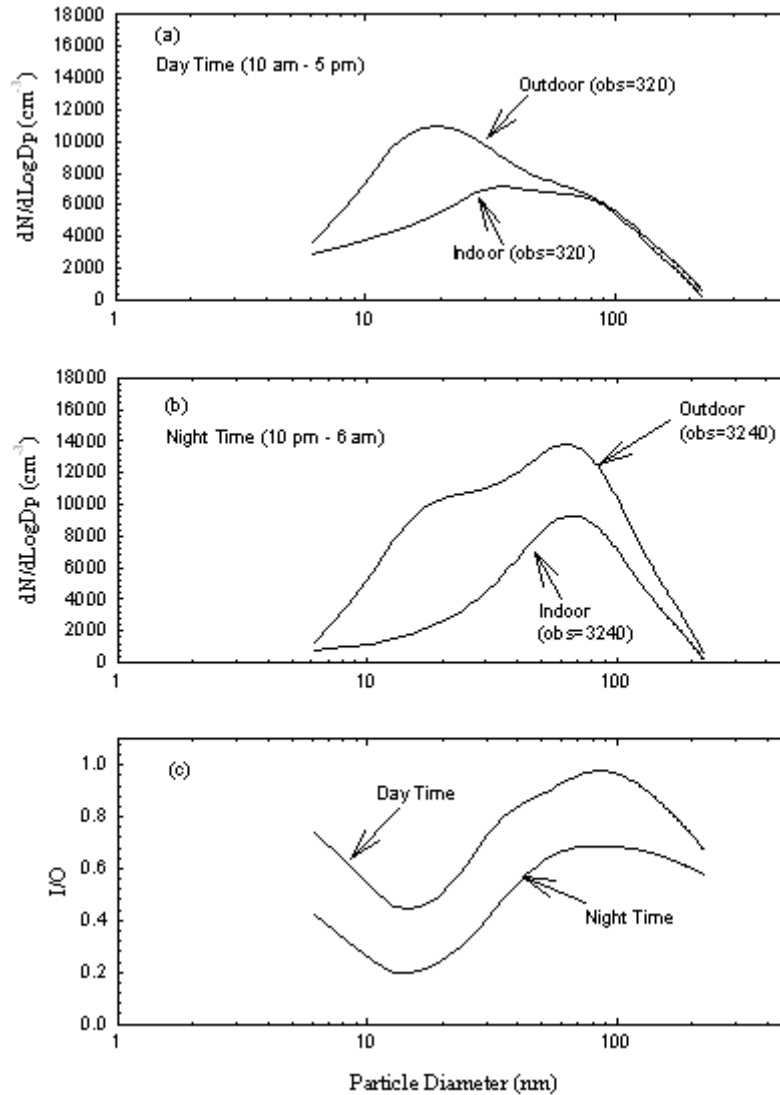


Figure 1. Averaged (a) day time, (b) night time outdoor and indoor particle size distributions and (c) size dependant I/O ratios in Apt 1. Number of observations is given in parentheses.

A daytime outdoor particle size mode near 20 nm was observed outside of apartment 1, consistent with previous reports (Zhu et al., 2002b). No such mode exists for indoor observations, and the indoor particle number concentrations are much lower and more stable than outdoors. Nighttime particle number concentrations, shown in figure 1(b), are comparable to their daytime values. Although traffic densities are lower during the night, vehicle speeds on the freeway are much faster. It has been shown previously that faster vehicles generate more particles (Zhu et al., 2002b). Lower nighttime temperatures, may also result in higher emission factors for particle numbers, as shown previously (Kittelson, 1998b). Yet another reason for higher particle number concentrations during the night may be lower wind speeds and a lower atmospheric mixing height at night, thus weaker atmospheric dilution effects. Wind was also more parallel to the freeway during the night, and therefore apartments close to both edges of the I-405 received large amounts of freeway aerosols.

As figure 1(c) shows, I/O ratios during day and night times exhibit similar trends and shapes. The difference between day and night I/O is due to higher air exchange rates during daytime. Day and night I/O profiles for particles above 20 nm are consistent with theoretical curve shapes. Curves for particles below 20 nm do not correspond to the accepted theory, as no downward trend is observed for both day and night time observations. These results may be affected by low instrument detection limits, and thus have less statistical confidence. Particle volatility may also explain why the I/O ratio increases for very small particles. Freeway ultrafine particles are known to have a large fraction of volatile components, especially for particles below 50 nm (Kittelson, 1998a). For example, some of the particles in the 20-40 nm size range may lose their volatile components and become particles of 20 nm or less as observed by Kuhn et al. (2004). Such loss of volatile components has been reported previously (Lunden et al., 2003).

Measurements were made under three ventilation conditions: closed window with the fan off (A), closed window with the fan on (B), and open window with the fan off (C). Averaged I/O size-dependent particle concentration ratios and their standard deviations for the three ventilation conditions are shown in figure 2. Under natural conditions (2a), the curve exhibits a similar shape as I/O ratio curves in figures 1, with an expected downward trend for particles greater than 20 nm, and an uncharacteristic upward trend for smaller particles. Under mechanical ventilation (2b), much lower I/O ratios are observed. This may be due to some partial filtering of the air entering the building by the ventilation system, which would decrease indoor particle concentration. The fan effect also diminishes the increase in I/O ratio for particles below 20 nm, as observed under natural ventilation conditions. With an open window (2c), the I/O ratio is very close to 1.0 across all particle sizes.

In summary, particle number concentration I/O ratios showed strong dependence on particle sizes and were influenced by different ventilation mechanisms. Under natural ventilation, the highest I/O ratios (0.6–0.9) were usually observed for larger ultrafine particles (70-100 nm), while the lowest I/O ratios (0.1–0.4) occurred typically around 10-20 nm. The size distributions of indoor aerosols showed less variability than those of outdoor freeway aerosols.

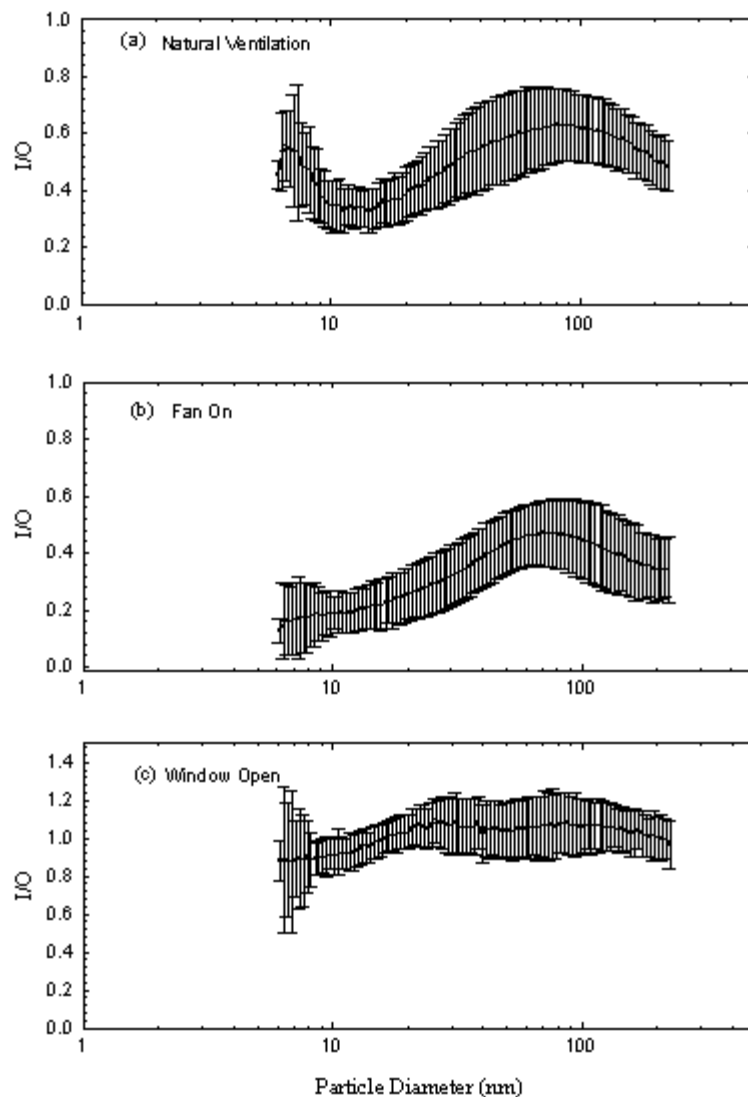


Figure 2. Averaged size dependant I/O ratios and standard deviations under different ventilation conditions in Apt. 1. (a) natural ventilation (b) fan on and (c) window open

References:

- Kittelson, D.B., 1998a. Engines and Nanoparticles: A Review. *Journal of Aerosol Science*, 29: 575-588.
- Lunden, M.M. et al., 2003. The transformation of outdoor ammonium nitrate aerosols in the indoor environment. *Atmospheric Environment*, 37(39-40): 5633-5644.
- Zhu, Y., Hinds, W.C., Kim, S., Shen, S. and Sioutas, C., 2002a. Study of Ultrafine Particles near a Major Highway with Heavy-duty Diesel Traffic. *Atmospheric Environment*, 36: 4323-4335.

Zhu, Y., Hinds, W.C., Kim, S. and Sioutas, C., 2002b. Concentration and size distribution of ultrafine particles near a major highway. *J Air Waste Manag Assoc*, 52(9): 1032-42.

9. Volatility of freeway ultrafine particles in outdoor and indoor environments

Introduction

Although recent studies have shown a positive association of exposure to ultrafine particulate matter (PM) with adverse effects on human health, it is not yet clear which PM components or properties of these particles may cause these responses. In the context of human exposure, an appreciable fraction of the indoor ultrafine aerosol is of outdoor origin, and elevated ultrafine particle concentrations have been reported near major highways (Zhu et al., 2002), where many urban residents live. Hence, these residents may be exposed to potentially harmful ultrafine particles. Because people spend most of their time indoors (Jenkins et al., 1992), it is of interest to study transformation of outdoor aerosols after they penetrate into buildings. Particle volatility must be considered when evaluating penetration of outdoor particles indoors. Volatile aerosols of outdoor origin may decrease in size or evaporate entirely as they penetrate into the typically warmer indoor environment during the colder period of the year. The resulting physical and chemical changes of outdoor particles will likely affect their toxicity and are important metrics in the development of fundamental understanding of the toxicity of PM originating from vehicular emissions. Recent emissions testing in either dynamometer (Sakurai et al., 2003a,b) or on-road testing facilities (Kittelson et al., 2004) has shown that, depending on vehicle type, age and ambient conditions, over 90% of the particles by number and 10–30% by mass consist of more volatile material than others (known as semi-volatile), and upon heating, will partially evaporate.

This paper is a companion paper to the work presented by Zhu et al. (2004), which focuses on ultrafine particle size distribution and penetration efficiencies into indoor environments. In this study, we examined volatility of penetrating ultrafine outdoor particles, predominantly from freeway emissions, into indoor environments. A tandem differential mobility analyzer (TDMA) system was used to study particle volatility at two apartments, 15 m and 40 m downwind of the 405 Freeway in Los Angeles, CA. The first differential mobility analyzer (DMA) selected particles of a certain diameter and subsequent heating of this monodisperse aerosol allowed for detection of changes in particle diameters by measuring the resulting size distribution with a second DMA. Both papers have been submitted to *Journal of Aerosol Science*.

Methods

The tandem DMA (TDMA) system used to measure volatility of particles is shown in Figure 1. The system was operated inside an apartment. The two Scanning Mobility Particle Sizers (SMPS, TSI model 3936) consisted of a bipolar charger (with an ^{85}Kr source), a long DMA (model 3081), and a Condensation Particle Counter (CPC, TSI model 3022A). The first SMPS (SMPS1) sampled either from outside the apartment or from inside. SMPS1 was set to select particles of a certain narrow size range. The resulting monodisperse aerosol was split into two streams. One stream went into the CPC of SMPS1 (control CPC), which measured the concentration of this monodisperse aerosol. The other stream traveled through a heater unit.

After passing through the heater, the conditioned aerosol went through the second SMPS (SMPS2), which measured its size distribution.

The heater used to condition aerosols consisted of a 50 cm, straight stainless steel tube with inside diameter of 5.4 mm. Part of the tube (40 cm) was wrapped with a 125 W rope heater and insulated with a fiberglass blanket around the tube and the rope heater. Heater dimensions were similar to the system described by Orsini et al. (1999). The aerosol temperature was measured using a thermocouple probe at the center of the flow in the tube, introduced through a hole in the side of the tube just downstream of the heated section.

Freeway 405 runs generally north and south along the apartment buildings. I-405 has ten lanes near the sampling location, five north bound and five south bound. The freeway is on the same level as the surrounding terrain of the sampling site. The apartments lie approximately 6 km to the east of Santa Monica Bay and the Pacific Ocean.

The study took place from December 2003 to January 2004. Measurements in the two apartments were performed during the day between 10am and 7pm. Apt. 1 was sampled for eleven days between December 19, 2003 and January 6, 2004, and measurements in Apt. 2 were completed in six days, between January 7 and 12, 2004.

For heating, the aerosol temperatures of 60 °C and 110 °C were chosen to determine ultrafine particle volatility. We expected most of the volatile material, for example sulfate and nitrate (Philippin et al., 2004), and organics, to evaporate at 110 °C. The temperature of 60 °C was selected to represent an intermediate state of volatilization. Other temperatures, 90 °C and 130 °C, were used to study the temperature dependence of the outdoor freeway aerosol.

Measurements

Figure 2 shows typical results from measurements of outdoor particles in Apt1 (15 m from freeway). The figure shows three normalized number size distributions: the first represents the selected monodisperse aerosol without conditioning (no heating) at ambient temperature; the second shows the size distribution of the original monodisperse aerosol after its heating to 60 °C; the third shows the size distribution after heating the aerosol to 110 °C. The size distributions were initially normalized using the measured concentration of the control CPC to account for changes in the ambient particle concentrations. In addition, the distributions were normalized so that the size distribution of the monodisperse aerosol without conditioning exhibited a maximum at one.

These measurements show that the mode diameter d_m of the originally monodisperse aerosol shifts towards a smaller diameter with increasing heater temperature. The mode also broadens with increasing temperature because not all particles shrink at the same rate due to differences in their composition.

To study temperature dependence more in detail, for particles with diameters of 18 nm, 27 nm, 45 nm, and 90 nm the mode diameter was determined from measurements at aerosol conditioning temperatures of 30 °C, 60 °C, 90 °C, 110 °C, and 130 °C. Figure 3 shows the mode diameter shift (mode decrease) Δd_m as a function of aerosol temperature resulting from these measurements, where Δd_m is the difference of the measured mode diameter to the selected particle diameter. The trend observed in this figure indicates that for temperatures of up

to 130 °C the diameter of all particles studied here (18 nm to 90 nm) is still shrinking. If a non-volatile core exists, then it will have a smaller diameter than that reached by particles at 130 °C (approximately half the diameter of the respective aerosols at ambient temperature). Figure 4 compares the decreasing mode diameters at 60 °C and 110 °C for particles sampled from outdoor and indoor environment, respectively. The mode diameter decreases more for outdoor particles.

The particle number size distributions can be integrated to give the total number concentration. By comparing the total number concentrations of heated aerosols to the total number concentration of the aerosol at ambient temperature, one can see whether heating results in particle losses. Normalized total number concentrations were obtained by integrating size distributions normalized with the control CPC average concentrations to account for changes in particle number concentration of the sampled aerosol during the measurements. To evaluate the losses, ratios Φ_N were calculated by dividing normalized total number concentrations for heated aerosols by the normalized total number concentrations of the aerosol at ambient temperature. Similarly, ratios Φ_V were calculated by dividing normalized total volume concentrations for heated aerosols by the normalized total volume concentrations of the aerosol at ambient temperature. The ratios Φ_N and Φ_V represent, the fraction of the aerosol that is not lost due to volatilization, hence describing losses in terms of number concentration and volume respectively.

In most cases heating did not result in significant particle number losses. Only 18 nm particles heated to 110 °C were lower in number concentrations than those at ambient temperature ($\Phi_N = 0.46 \pm 0.27$). These results may be due to particles' complete volatilization or shrinkage to sizes below the CPC's detection limit of approximately 7 nm.

As indicated by the fractions Φ_V shown in Table 1, volume losses increase significantly from 60 °C to 110 °C, and are higher for outdoor than indoor particles. Again, this indicates that outdoor particles are more volatile than indoor particles. Smaller particles are also shown to lose more of their volume, indicating that they may be composed of less non-volatile material.

Outdoor particle size distributions of ambient and heated aerosols were also measured in Apt. 2, to evaluate changes of the volatility properties at a greater distance from the freeway. When results are compared between Apt. 1 and Apt. 2, further from the freeway (Apt. 2), the size distribution at 110 °C shows a less distinct and a broader mode. This implies that particles further from the source may experience greater external mixing.

The mode decreases of outdoor aerosol at Apt. 2 seem to be similar for 18 nm and 27 nm aerosols and lower for 45 nm and 90 nm aerosols when compared to mode decreases of outdoor aerosol at Apt. 1. The ratios Φ_N for the two apartments show for 60 °C no particle number losses due to heating at both apartments, whereas at 110 °C losses at Apt. 2 are lower (Φ_N closer to one) than losses at Apt. 1. Volume losses show the same decreasing trend at increased distance from the freeway as the number losses. Again, the decreasing volatility is more evident at the larger particle sizes.

Summary

Volatility properties of freeway ultrafine outdoor and indoor aerosols were examined by heating particles and detecting changes in their diameters and number concentrations. Results from this study suggest that outdoor particles are more volatile than indoor aerosols, for all studied particle

diameters. Although the aerosol mode diameter broadened for both indoor and outdoor particles, increase in temperature resulted in greater mode decreases for outdoor aerosols. In addition, outdoor particles lost more of their volume upon heating than their indoor counterparts. Measurements of particle number concentrations revealed that more of outdoor than indoor particles were completely volatilized at 110 °C. At 60 °C heating did not result in significant particle losses for both indoor and outdoor aerosols.

Bi-modal distributions were observed for outdoor 90 nm and 45 nm particles heated to 110 °C. These distributions indicate that a fraction of the aerosol is composed of mainly non-volatile particles, whereas the rest is mainly volatile and therefore shrinks. No bi-modal distribution was observed for 18 nm and 27 nm particles, suggesting that all of these particles are composed of mainly volatile material.

Increasing temperature causes particles to shrink further. For instance, when heated to 130 °C, particles shrink to approximately half of their original size. A trend in the temperature dependence of the mode decrease indicates that a fraction of these heated aerosols might reach a final size, a non-volatile core.

Another sampling location, further away from the freeway, was chosen to evaluate outdoor particle volatility in relation to distance to the source. The study showed that aerosol volatility, for all studied particle diameters, decreases with increasing distance from the sources.

References

- Jenkins, P. L., Phillips, T. J., Mulberg, E. J., Hui, S. P., 1992. Activity patterns of Californians—use of and proximity to indoor pollutant sources. *Atmos. Environ. A-Gen.* 26 (12), 2141–2148.
- Kittelson, D. B., Watts, W. F., Johnson, J. P., 2004. Nanoparticle emissions on Minnesota highways. *Atmos. Environ.* 38 (1), 9–19.
- Orsini, D. A., Wiedensohler, A., Stratmann, F., Covert, D. S., 1999. A new volatility tandem differential mobility analyzer to measure the volatile sulfuric acid aerosol fraction. *J. Atmos. Ocean. Technol.* 16 (6), 760–772.
- Philippin, S., Wiedensohler, A., Stratmann, F., 2004. Measurements of non-volatile fractions of pollution aerosols with an eight-tube volatility tandem differential mobility analyzer (VTDMA-8). *J. Aerosol Sci.* 35 (2), 185–203.
- Sakurai, H., Park, K., McMurry, P. H., Zarling, D. D., Kittelson, D. B., Ziemann, P. J., 2003a. Size-dependent mixing characteristics of volatile and nonvolatile components in diesel exhaust aerosols. *Environ. Sci. Technol.* 37 (24), 5487–5495.
- Sakurai, H., Tobias, H. J., Park, K., Zarling, D., Docherty, S., Kittelson, D. B., McMurry, P. H., Ziemann, P. J., 2003b. On-line measurements of diesel nanoparticle composition and volatility. *Atmos. Environ.* 37 (9–10), 1199–1210.
- Zhu, Y., Hinds, W. C., Krudysz, M., Kuhn, T., Froines, J., Sioutas, C., 2004. Penetration of freeway ultrafine particles into indoor environments: I. Ultrafine particles and co-pollutants. *J. Aerosol Sci.* (submitted).
- Zhu, Y. F., Hinds, W. C., Kim, S., Sioutas, C., 2002. Concentration and size distribution of ultrafine particles near a major highway. *J. Air Waste Manage. Assoc.* 52 (9), 1032–1042.

Tables

Table 1: Fractions Φ_V for outdoor and indoor aerosols at Apt. 1.

d_p	Φ_V outdoor [nm]		Φ_V indoor [nm]	
	60°C	110°C	60°C	110°C
18 nm	0.73 ± 0.20	0.21 ± 0.09	0.77 ± 0.14	0.22 ± 0.08
27 nm	0.63 ± 0.04	0.18 ± 0.06	0.90 ± 0.06	0.32 ± 0.06
45 nm	0.85 ± 0.13	0.34 ± 0.02	0.94 ± 0.08	0.40 ± 0.03
90 nm	0.85	0.41 ± 0.01	0.99	0.58 ± 0.03

Figures

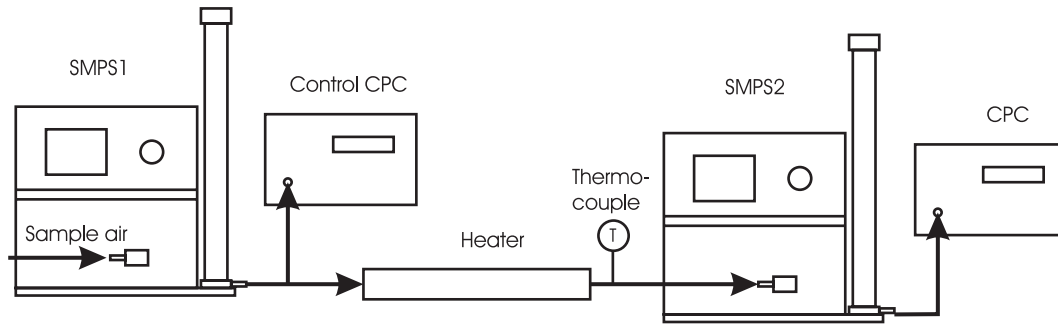


Figure 1: Tandem DMA Set-up

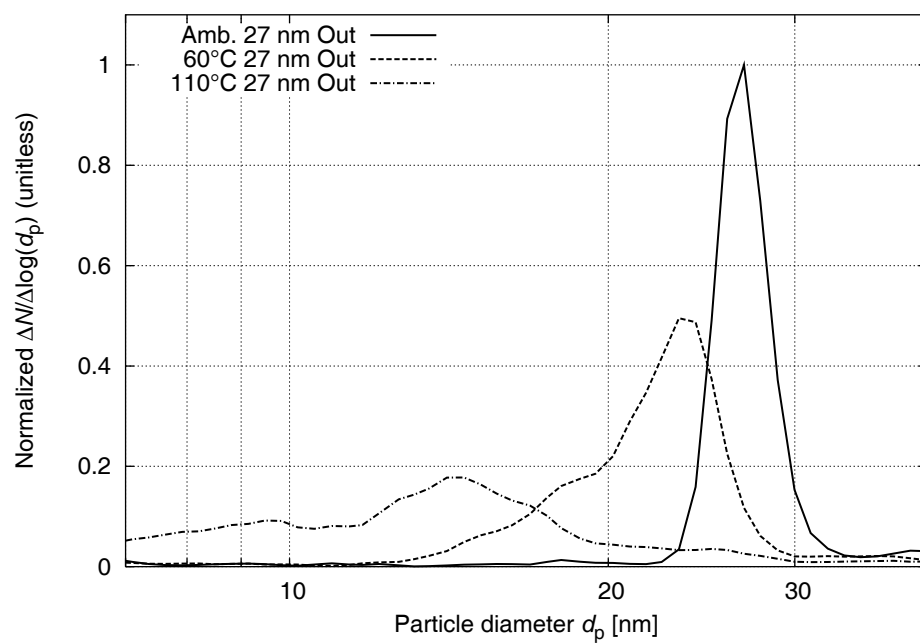


Figure 2: Normalized number size distribution of 27 nm outdoor particles at a distance of 15 m from the freeway 405 freeway at ambient temperature (~ 25 °C) and after conditioning (heating) at 60 °C and 110 °C.

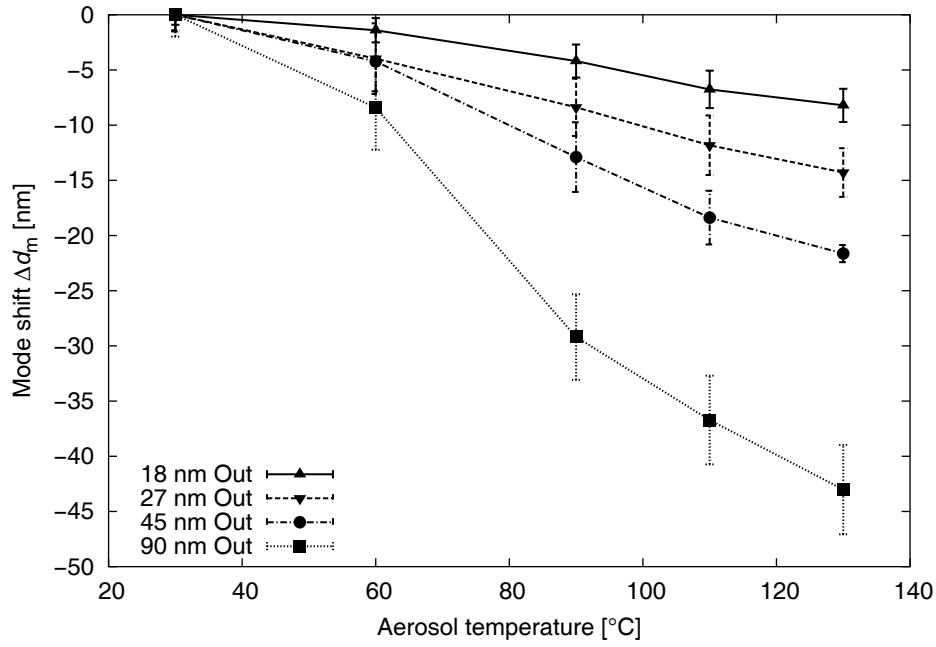


Figure 3: Mode diameter shift Δd_m as a function of aerosol conditioning temperature. The error bars for the 45 nm and 90 nm particles are standard deviations from four measurements on different days. For 18 nm and 27 nm particles, only two and one measurements, respectively, were performed, hence the error bars for these two sizes represent modes widths (at half amplitude).

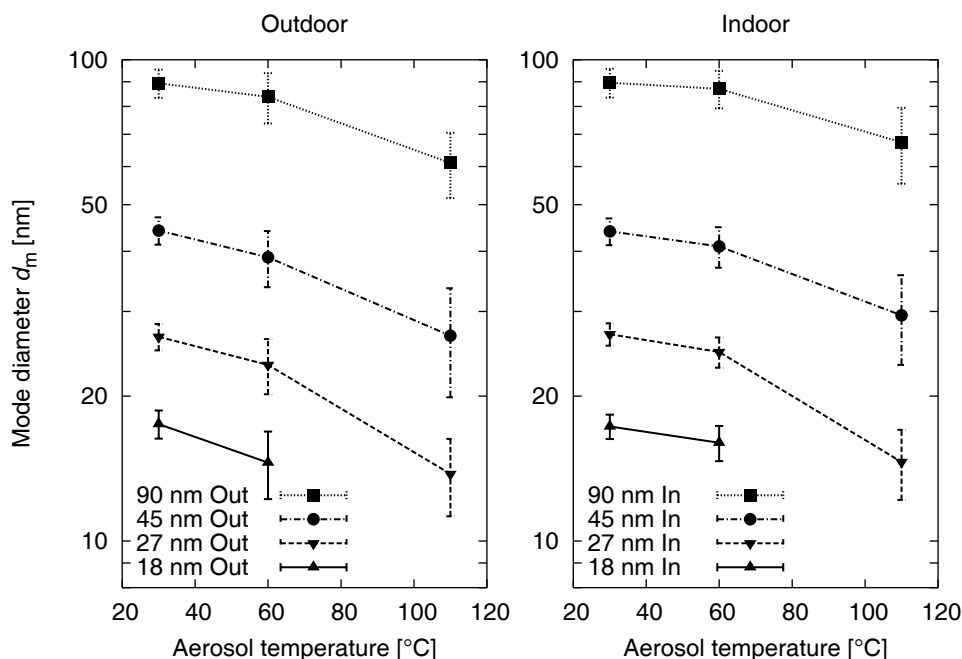


Figure 4: Mode diameters d_m as a function of temperature for 18 nm, 27 nm, 45 nm, and 90 nm Apt. 1 outdoor and indoor particles. Averages were obtained based on three or four measurements for all particle sizes except the following: 45 nm indoor and outdoor aerosols heated to 110 °C, and 27 nm indoor particles at 110 °C were calculated based on only two measurements. Error bars indicate mode widths at half amplitude of the average size distribution, demonstrating mode broadening with increasing temperature.

10. Analysis of Size- and Time-Resolved Particulate Measurements

Susanne Hering, Aerosol Dynamics Inc.

Our current efforts are focusing on the analysis of the size distributions collected with the cascaded nitrate and carbon systems, with comparison to the physical size distributions measured by a combination of SMPS and Aerodynamic Particle Sizing. Our objectives are (1) to ascertain whether the changes in the size distribution for particulate nitrate are reflected in changes in total physical size distribution (2) to understand the relationship between particle size and meteorology. Specifically, we wish to understand those conditions conducive to formation of nitrate in the condensational mode ($<0.45\mu\text{m}$), droplet mode (0.5 to $1\mu\text{m}$) and coarse mode (1 - $2.5\mu\text{m}$) respectively.

In our prior reports we have noted that $\text{PM}_{2.5}$ carbon is consistently dominated by the “condensational” mode while $\text{PM}_{2.5}$ nitrate tends more toward the droplet mode. In the spring, summer and fall the nitrate size distribution most often shows a dominance of the droplet mode

over the condensational mode. During the winter months the nitrate condensational and droplet modes tend to be equally important.

We previously identified the periods listed in Table 1 as ones of specific interest for analysis in concert with the physical size distribution data. We have now synthesized the physical size distribution, cascaded nitrate and cascaded carbon into a single data set, utilizing one-hour averages of the data. For each of the three size ranges, we calculate a reconstructed particle mass as: $M_R = 1.3(\text{NO}_3^-) + 1.4(\text{C})$, where the multipliers are to account for associated cations for nitrate, or for associated hydrogen and oxygen for the carbon mass.

Graphs comparing M_R with the physical volume within each of the three size modes measured by the cascaded ICVC system are shown for in Figure 1 and 2 for two of the periods identified in Table 1. As is apparent, the reconstructed mass tracks and physical aerosol volume track well for the droplet and condensational mode size ranges. Volume and mass values are fairly comparable. Correlation coefficients and regression slopes are listed in Table 2. For the droplet mode, the reconstructed mass derived from nitrate and carbon alone accounts for most of the measured aerosol volume, yielding regression slopes of 1.3 g/cm^3 to 1.4 g/cm^3 . For the coarse portion of $\text{PM}_{2.5}$, for which one expects a soil dust contribution, the nitrate and carbon sum is correspondingly less than the volume from the physical measurements.

In Figure 3 we plot the ratio of nitrate to carbon for the two for the condensational ($0.1\text{-}0.45 \mu\text{m}$) and droplet ($0.45\text{-}1\mu\text{m}$) size fractions. These data show remarkable variability between the October and February time periods. In October, the condensational mode is dominated by carbon, while the droplet mode is dominated by nitrate. In the February time frame the dominance of nitrate often dominates both size fractions. These differences, and the associated underlying dynamics, will be interesting to pursue.

Table 1. Periods of Interest for Particle Size Distribution Analysis.

Dates	Nitrate	Particulate Carbon
Oct 11- 21, 2001	Droplet mode dominates on most days, but coarse and condensational modes both significant	Dominated by condensational mode, very little coarse
Jan 16-22, 2002	Droplet and condensation modes comparable	Dominated by condensational mode
Feb 6 - 26, 2002	Large coarse mode on Feb 7, otherwise droplet and condensation comparable.	Large coarse on Feb 7, otherwise condensational mode dominated.
Mar 28 - April 4, April 10 - 15	Droplet mode becomes dominant	While condensational mode still dominant, the droplet mode is more important.

Table 2. Comparison of the Reconstructed Mass Associated with Nitrate and Carbon, and the Aerosol Volume derived from Physical Size Distributions**a. Square of the Correlation Coefficient**

Particle Size Range	Oct 11- 20, 2001	Feb 6 - 26, 2002
0.1-0.45 μm	$R^2 = 0.92$	$R^2 = 0.86$
0.45 - 1.0 μm	0.86	0.88
1.0 - 2.5 μm	0.81	0.35

b. Regression Slopes (g/cm^3)

Particle Size Range	Oct 11- 20, 2001	Feb 6 - 26, 2002
0.1-0.45 μm	1.01	0.78
0.45 - 1.0 μm	1.26	1.42
1.0 - 2.5 μm	0.57	--

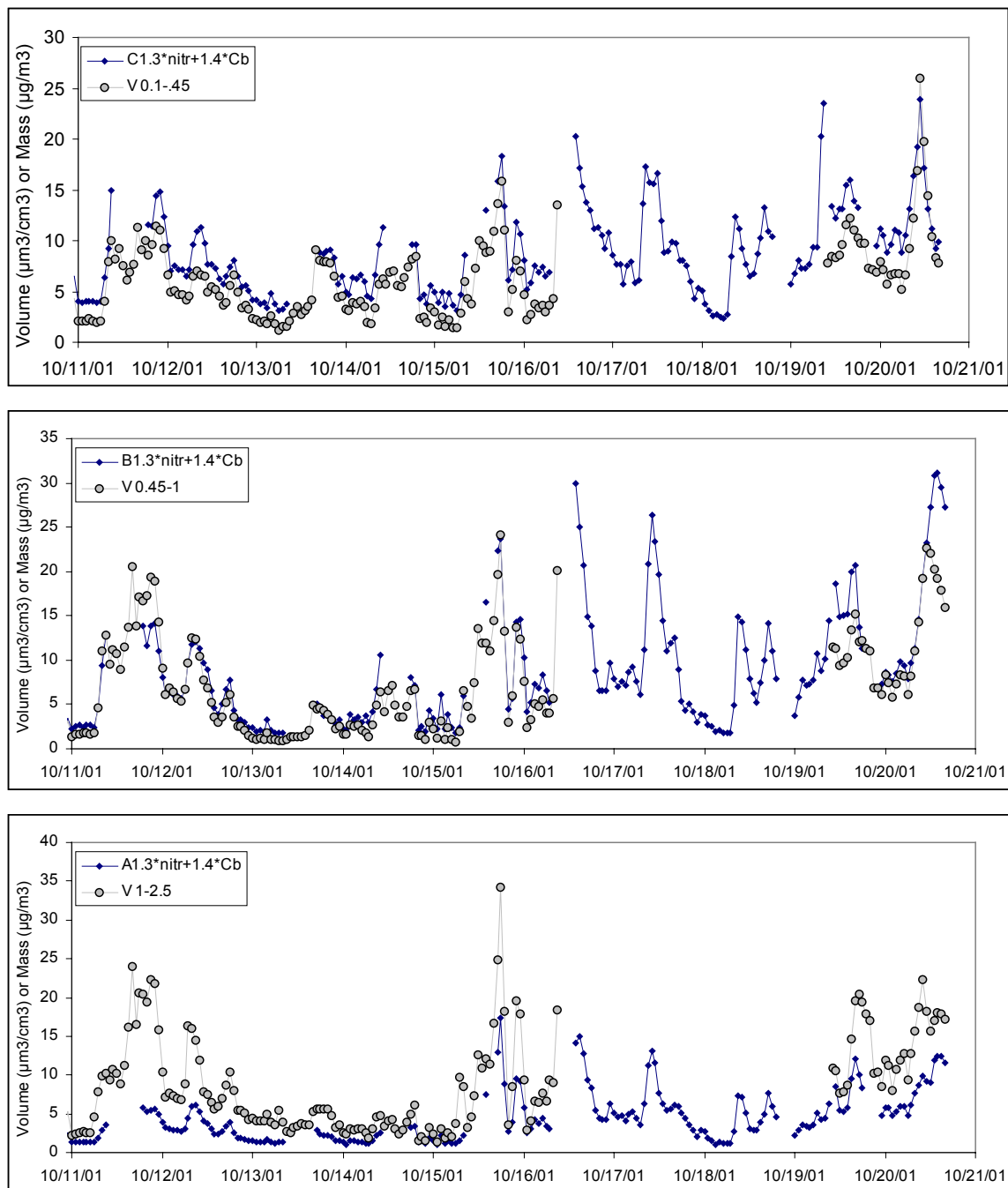


Figure 1. Comparison of the reconstructed aerosol mass derived from nitrate and carbon mass concentrations to the aerosol volume from the physical size distribution measurements for each of the three size fractions: 0.1-0.45 μm , 0.45-1 μm and 1-2.5 μm for the October 2001 time period.

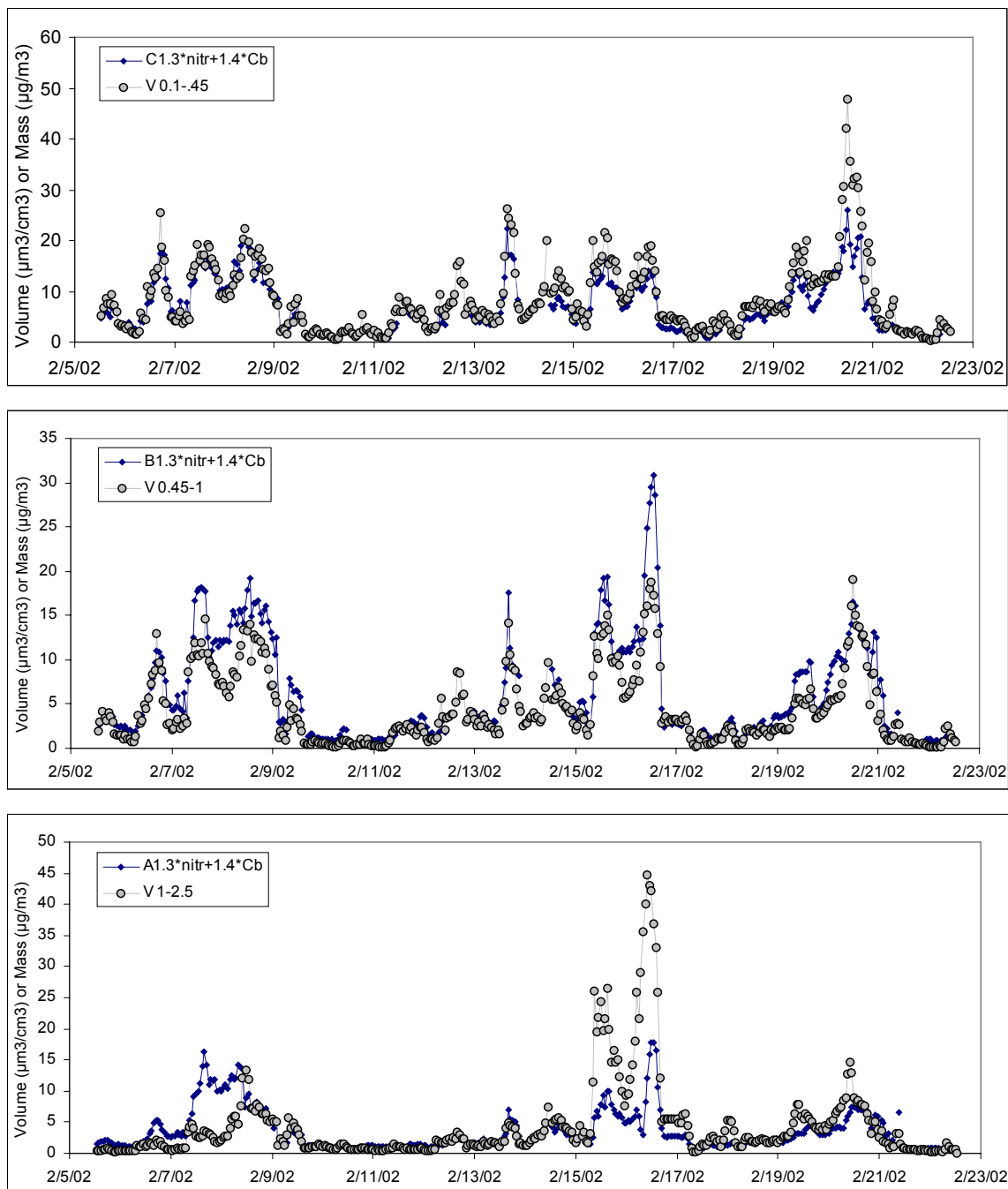


Figure 2. Comparison of the reconstructed aerosol mass derived from nitrate and carbon mass concentrations to the aerosol volume from the physical size distribution measurements for each of the three size fractions: 0.1-0.45 μm , 0.45-1 μm and 1-2.5 μm for the February 2002 time period.

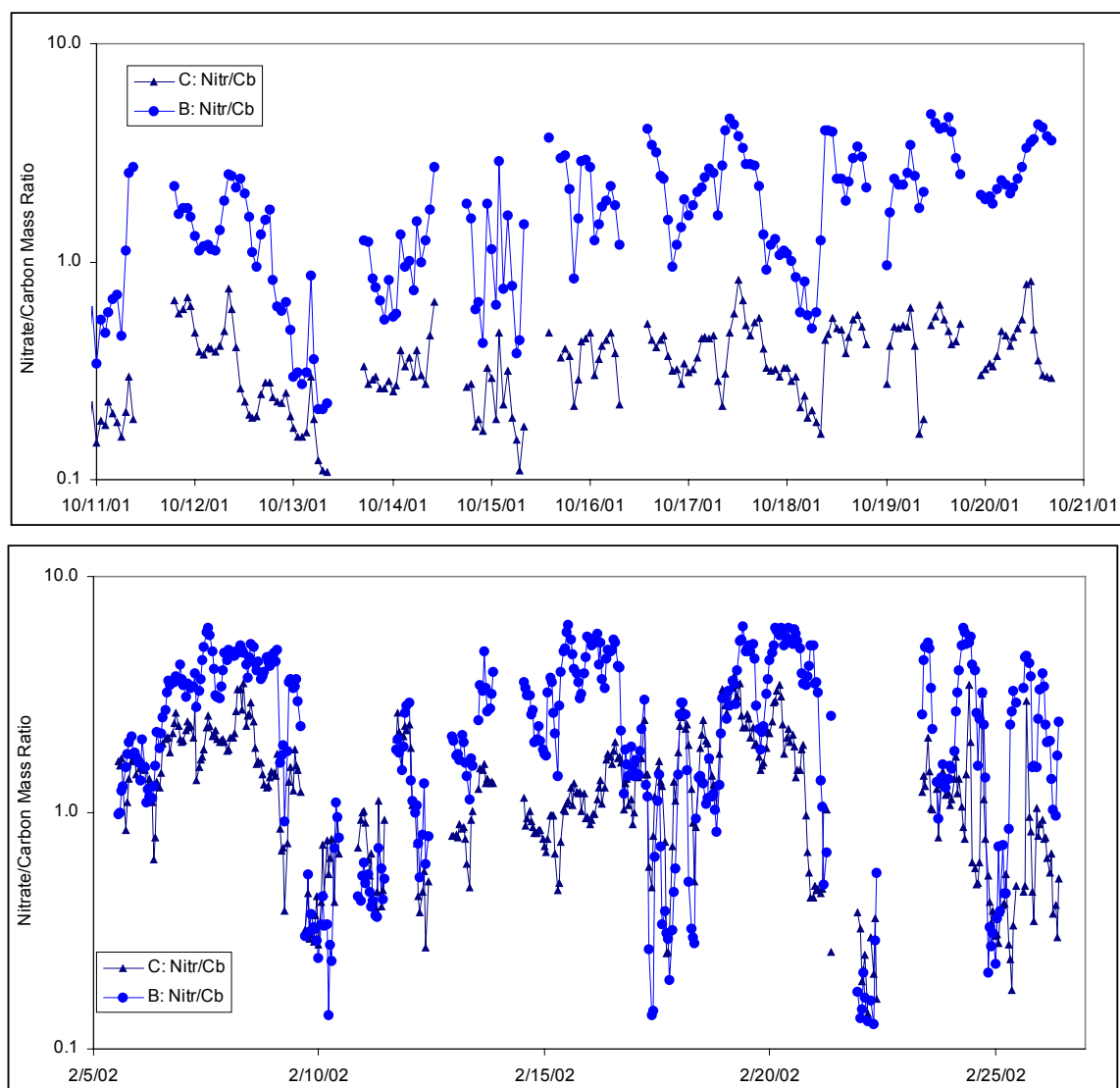


Figure 3. Nitrate to carbon mass for the condensational (0.1-0.45 μm) and droplet (0.45-1 μm) size fractions, showing the dominance of nitrate in the droplet mode for most periods.